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THE JOURNAL OF

INDUSTRIAL AND ENGINEERING CHEMISTRY

PUBLISHED MONTHLY BY THE AMERICAN CHEMICAL SOCIETY

Vol. 12, No. 7 JULY, 1920 $6 per Year

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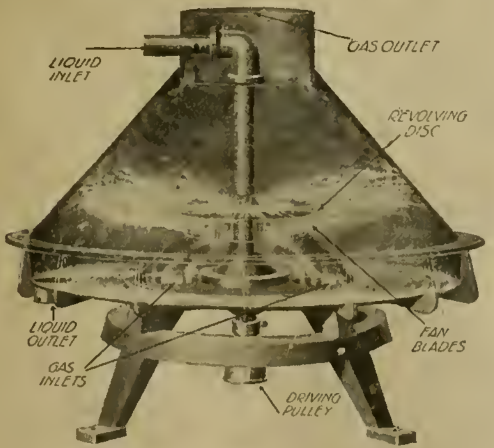

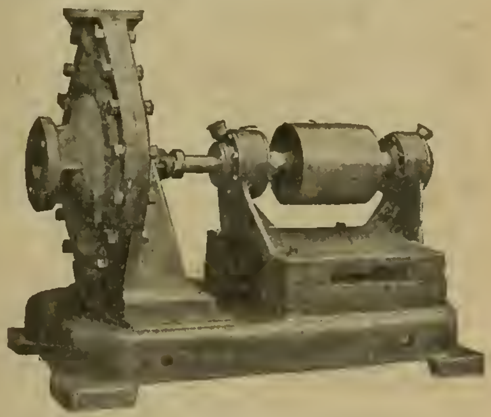

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Alphabetical List of Advertisers, page 86 Table of Contents, page 625 Classified Directory, pages 36-38-40-42

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CONTENTS

EDITORIALS:

Rope Making.......... 626
Canadian Hospitality.......... 626
One-Sided Greasing.......... 626
An Unfinished Story.......... 627
Notes.......... 628
RESPONSIBILITIES OF THE CHEMIST AS A CITIZEN. H. W. Jordan.......... 629
CHEMICAL INDUSTRIES AND TRADE OF NORWAY. O. P. Hopkins.......... 632

ORIGINAL PAPERS:

Some Catalysts Which Promote Reaction between Aniline and Ethyl Alcohol. T. B. Johnson, A. J. Hill and J. J. Donleavy.......... 636
The Effect of Air in Steam on the Coefficient of Heat Transmission. C. S. Robinson.......... 644
The Production of Phosphoric Acid by Smelting Phosphate Rock in a Fuel-Fed Furnace. William H. Waggaman and Thomas B. Turley.......... 646
Investigations on Zirconium. J. W. Marden and M. N. Rich.......... 651
A Chemical Study of Frozen Fish in Storage for Short and Long Periods. E. D. Clark and L. H. Almy.......... 656
Solid Phases Obtained by the Evaporation of Certain Soil Extracts. M. S. Anderson and William H. Fry 663
Determination of Nitrate Nitrogen in Nitrates and Fertilizers. H. C. Moore.......... 669
A Direct Method for the Determination of Rubber Hydrocarbon in Raw and Vulcanized Rubber. W. K. Lewis and W. H. McAdams.......... 673
Method for the Determination of Thiocyanates in Ammoniacal Liquor and Waste Liquor from Ammonia Stills in the By-product Coking Industry. Joseph A. Shaw.......... 676
Volumetric Method for the Determination of Diastatic Capacity. J. T. Flohil.......... 677
The Uniform Composition of Commercial "Stearic" Acids, and Its Explanation. Ben H. Nicolet.......... 677

LABORATORY AND PLANT:

Photobibliographic Research Methods—The Compilation of Technical Data with the Aid of Photography. Arthur Worischek.......... 679
Potash From Kelp. II—The Experimental Distillation of Kelp at Low Temperatures. G. C. Spencer. 682
Tar-Still Operation in Hardwood Distillation Plants. L. F. Hawley and H. N. Calderwood, Jr.......... 684
The Hess-Ives Tint-Photometer and Its Use with Raw Sugars. George P. Meade and Joseph B. Harris.......... 686
Preservatives for Fermentable Beverage Samples. J. S. McCune and A. N. Thurston.......... 689
A Simple Alcohol-Testing Device. Sigmund Waldbott. 690

ADDRESSES AND CONTRIBUTED ARTICLES:

A Plan for Incentive to Research in Pure and Applied Chemistry. William J. Hale.......... 690
The Relation of the Chemist to the United States Pharmacopoeia. Charles H. LaWall.......... 696

WILLARD GIBBS MEDAL AWARD:

Presentation Address. W. R. Whitney.......... 697
Medal Address. International Scientific Relations. F. G. Cottrell.......... 697

CHEMICAL READING COURSES:

Elementary or Introductory Chemistry.......... 701
Household Chemistry.......... 702
General and Physical Chemistry.......... 702
Inorganic and Analytical Chemistry.......... 704

SCIENTIFIC SOCIETIES:

In the Alembic of Publicity; Convention of Canadian Chemists; Report of the Committee on Cottonseed Products, Division of Industrial and Engineering Chemistry, American Chemical Society; Annual Meeting of the Division of Chemistry and Chemical Technology, National Research Council; Presentation of Honorary Membership Certificate to M. Ernest Solvay; U. S. Pharmacopoeial Convention, Centennial Meeting; Manufacturing Chemists' Association; Calendar of Meetings.......... 705

NOTES AND CORRESPONDENCE:

Unsaponifiable Matters; Awards for Theses on Foods and Beverages; The Industrial Fellowships of the Mellon Institute; Conservation of Standard Samples of the Bureau of Standards.......... 713
OBITUARY.......... 718
WASHINGTON LETTER.......... 718
INDUSTRIAL NOTES.......... 719
PERSONAL NOTES.......... 721
GOVERNMENT PUBLICATIONS.......... 722
BOOK REVIEWS.......... 725
NEW PUBLICATIONS.......... 726
MARKET REPORT.......... 727

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EDITORIALS

ROPE MAKING

Tearing to pieces a bit of hemp rope may indicate summer idling, but it has induced two thoughts—first, the individual bast fibers stand out preëminently as strong, hardy vegetable cells; second, the act of intertwining the individual fibers produces a rope of a strength multifold that of the sum of the individual fibers. What has this to do with chemistry? Quite a bit, in the light of coming events.

During the summer and early fall of 1921 four strong chemical organizations will hold their annual meetings in America, namely, the Society of Chemical Industry (British), the Convention of Canadian Chemists, the American Chemical Society, and the Seventh National Exposition of Chemical Industries.

These are all lusty bast fibers, each strong in itself as such strength goes, and there they lie individually on the table of 1921. Let's get at the business of rope making, and thereby fashion for the Anglo-Saxon world a binding power which will hold fast for our respective countries those new chemical industries which have developed because of the war and whose importance to the national welfare cannot be overestimated.

Why not bring these meetings together, and thereby enable all to partake of the benefits of such a gathering of Anglo-Saxon chemists? It is recognized, of course, that exposition week is an unfortunate time for scientific gatherings, for the distractions of the Exposition militate against a successful scientific program, but the whole problem could be solved if the American Chemical Society would hold its annual meeting a week or two later than usual, and the British organization could postpone its visit to this country until September, 1921. Our Canadian friends would certainly enjoy New York more in September than during the heated spells of July. On the basis of a two weeks' program it would be possible for all to share in the meetings of the chemical societies, and to attend the Exposition. At the same time, the opportunities for informal conferences and mutual acquaintance during exposition week would make possible a meeting to immediately follow the Exposition which would bring to more definite conclusion many policies which would be originated and informally discussed during the early days of the joint gathering. Aside from the visits to the Exposition, that week would offer exceptional opportunity to our British and Canadian guests to visit in small groups many of the industrial plants in the vicinity of New York City. The journey to Canada at the closing of such an eventful gathering would attract many. Thus would strength be increased multifold by this intertwining of chemical forces.

It is remarkable how similar are the problems affecting chemistry in our three countries. There is the same fundamental need of public understanding of what our efforts mean; there is the same consequent difficulty in securing favorable legislative action; salaries are inadequate in all alike; progress during the last four years has been appreciably the same. Much still remains to be done. 1921 offers a great opportunity.

As a coördinating agency in this matter, we would suggest that the officers of the Chemical Exposition take this subject up at once with the officers of the several organizations concerned with a view to making such adjustments as will assure this joint gathering. Thus would be assembled a large group of chemists, inspired with the common purpose of making the Anglo-Saxon race supreme in the field of chemistry, to take part in deliberations which should prove historic for our science.

CANADIAN HOSPITALITY

At the recent joint annual meeting of the Canadian Section of the Society of Chemical Industry and the Canadian Institute of Chemistry, it was our good fortune to be the guest of Canadian chemists. Those last few words tell a story of most delightful hospitality, of charming entertainment, and of unaffected good fellowship. The meeting furnished opportunity for seeing Canadian chemists in vigorous action, progressive, wide-awake, developing policies suited to conditions of their country, and imbued through and through with a spirit of patriotic devotion. We can never forget the experience. We understand now the glorious record of Canadian soldiers throughout the war. And the long boundary line from the Atlantic to the Pacific has and needs no military guard of either nation.

ONE-SIDED GREASING

The National Prohibition Act is a two-wheeled cart, and not a monocycle. It provides against the use of alcohol as a beverage and at the same time in specific terms declares that the use of alcohol in research and in the industries is to be encouraged and facilitated. The Volstead Act exists for enforcing the provisions of the Prohibition Act and for carrying out the intent of Congress. One wheel of this cart, the prohibition side, has been abundantly greased and is running smoothly and efficiently in spite of the obstacles deliberately thrown in the roadway, while the other wheel has received but scant attention. It is screaking badly and friction is developing.

In such situations this friction usually finds its expression in loud-mouthed complaints, but fortunately that does not hold true in the present case. There is always a spirit of coöperation hovering around, if we only try to find it. It has been found in the case of alcohol for research and the industries. On June 17, 1920, there gathered in the office of the Commissioner of Internal Revenue in Washington, Lt. Col. Amos A. Fries of the Chemical Warfare Service, Mr. George W. Patterson, designated by Secretary Daniels to represent the Navy Department, representatives of the American Chemical Society, the Manufacturing Chemists' Association, the American Dyes Institute, the American Pharmaceutical Association, the American Drug Manufacturers' Association, the National Association of Retail Druggists, the National Whole-sale Druggists' Association, the Manufacturing Perfumers' Association, the Proprietary Association of America, the Drug Trade Conference, and individual manufacturers and users of industrial alcohol.

Owing to the illness of Commissioner Williams the hearing was conducted by Mr. Paul Myers, assistant to the Commissioner, in the presence of several officials of the Bureau. Brief addresses were made by the representatives present, the burden of which was that it was fully realized how pressing had been the problems before the Bureau in the administration of the Act, and how great an organization had had to be quickly built up. The great importance of alcohol in the chemical, pharmaceutical, and drug industries was clearly pointed out. Likewise the large demands of the Government for alcohol in smokeless powder and poison gas manufacture in time of war were demonstrated by the officials present. Statistics were exhibited showing the present greatly reduced output of alcohol.

In view of these representations it was urged that a special officer of the Bureau possessing technical qualifications be designated to have direct supervision of this feature of the Act. It was further suggested that if the Commissioner desired such aid, he invite the various national organizations to nominate representatives to an unofficial civilian board which would act in an advisory capacity to the Commissioner in working out satisfactory solutions of the various technical questions involved.

A fine spirit pervaded the meeting, and should the Commissioner adopt the suggestions made at the meeting the friction of that other wheel will be diminished, the industries will prosper, and the intent of Congress be fully carried out.

AN UNFINISHED STORY

Congress has adjourned. The expected "recess" instead of adjournment did not materialize. Satisfactory assurance from Democratic leaders that no attempt would be made to create political capital by a presidential reconvening of Congress, the call of the two great national conventions, and the desire of both Republicans and Democrats to get into the great American quadrennial game of president-making led to adjournment. The record as to legislation affecting directly the chemical industries is only a half-told tale.

First and foremost—the future existence of the Chemical Warfare Service is assured. Both Senate and House voted favorably upon its independent character, and in the conference committee the Senate members accepted the wording of the bill as it passed the House, defining the duties of the Service. This was important, for without it there would always have been the possibility of a sidetracking of the Service by departmental rulings. There remains only one matter of vital importance, the appointment of the Chief of the Chemical Warfare Service. The situation in regard to this is so clear, the individual with the necessary experience and demonstrated ability so easily recognized and so unique in the possession of these qualifications, that it is impossible to conceive of any other appointment by the Secretary of War and the Chief of Staff than that of Colonel Amos A. Fries, the present Chief of the Service. With Colonel Fries in command, bearing again the title of Brigadier General which he won in the field with the A. E. F., the enthusiastic coöperation of civilian chemists may be relied upon.

Second—The closely related dye bill remains in the position recorded in our last issue. The bill was not brought up for consideration by the Senate during the hurried closing days of the session. Senator Frelinghuysen, that indomitable fighter, read into the record an important communication from all of the smaller manufacturers of dyes, showing that the failure of Congress to enact adequate protective legislation for the industry would react destructively first upon these smaller manufacturers. Senator Wolcott of Delaware presented a lucid explanation of the Levinstein agreement, which showed that no world monopoly was contemplated or indeed possible under the agreement. The dye bill holds its place upon the Senate calendar, in position to be called up whenever the Senate desires during the short session beginning next December. At that time the same senators will be present to vote upon it, and, for the same reasons given in our last issue, we again predict that before this Senate adjourns finally on March 4, 1921, the dye bill will be passed and the industry thoroughly safeguarded. Meanwhile, the Sundry Civil Appropriation bill carries a significant item of $25,000 for the continuance of the work of the War Trade Board Section of the Department of State. The protection of the coal-tar chemical industry which has been afforded by the Trading with the Enemy Act since the blockade was raised will be maintained.

Third—The Bacharach bill never reached consideration by the Senate. It is a strange outworking that this Congress, controlled in both Houses by that party which has always boasted of its policy of protection for American industries, should have left without adequate protection, and for the most part on an absolutely free-trade basis, those industries which were called into being by the nation's need in time of war and upon the strong urging of officials of our Government. These industries, for which skilled labor has had to be developed in every department, must for the next few months rely solely upon the patriotic support of American consumers. There are to-day strange things going on which threaten their very existence.

Fourth—The Nolan bill, providing relief for the Patent Office, passed the Senate, but as it carried an amendment providing for assignment to the Federal Trade Commission of patents by government employees the bill had to go to conference, and there it remains, for the conductor was calling "All aboard for Chicago," and the engineer of the San Francisco special was getting up steam. We've seen the boys in college get just as badly demoralized just before a big football game. We always have maintained that campus life is but a miniature reflection of the greater world outside. Well, when it's all over we'll be as good Americans as ever, and our faith is still strong in the present Senate, though it surely is taking plenty of time to pass a few, plain, simple, necessary measures.

NOTES

It is with pleasure we announce that, beginning with the August issue, THIS JOURNAL will carry a monthly London letter from Dr. Stephen Miall, LL.D., B.Sc. Dr. Miall is the co-secretary and treasurer of the Federal Council for Pure and Applied Chemistry, and is also managing director of the Brimsdown Lead Company. It is hoped that through Dr. Miall's exceptional opportunity for close observation American chemists will be kept in touch with the thought and policy of British chemists and with the most recent developments in the field of industrial chemistry in Great Britain.

Announcement of the recess appointment of Professor Marston Taylor Bogert of Columbia University as a member of the Tariff Commission brings a comfortable feeling to all chemists. It has long been felt that the intricate character of the questions involved in the tariff as applied to chemicals demanded the presence on the Commission of one thoroughly familiar with matters chemical. Professor Bogert's high attainments in chemistry make his appointment an appropriate one. The country is under many obligations to him for patriotic service rendered throughout the war, and his work on the Tariff Commission will constitute a further obligation of this nature. Dr. Bogert has served as President of the American Chemical Society and of the Society of Chemical Industry. He represented chemistry at the original White House conference on conservation called by President Roosevelt. It is peculiarly fitting that one who is above all else an organic chemist should have been appointed to the Commission at a time when organic chemical industries are being so rapidly developed. Congratulations to both Dr. Bogert and the Tariff Commission.

It is a matter of rejoicing that Arthur Lachman has returned to his home in San Francisco none the worse for wear during his absence of several months while suffering from amnesia. In fact, he seems to have spent his time profitably, for according to a communication from a friend, he returned in the possession of a new suit of clothes and a hundred dollars earned in the automobile industry, which is a pretty good proof of chemical amnesia in these days. All of Dr. Lachman's friends join in the hope for a speedy recovery of his usual good health.

Synthetic camphor is rapidly finding its place on the map. From time to time references have been made in these columns to the necessity of the development of this industry as a measure of economic independence. It is welcome news that three of our most prominent chemical manufacturers are now engaged in the manufacture of camphor from spirits of turpentine, while we hear rumors of another project using a method which gives promise of very valuable results. From America's raw material America's supplies of camphor will be produced, thus gaining another step forward in the march of economic independence.

Honors are coming thick and fast to Dr. F. G. Cottrell, who organized the Research Corporation and assigned to it the patents on his process of electrical precipitation for the threefold purpose of insuring sound commercial development of the process, of dedicating its profits to scientific research, and of insuring his own freedom from the usual business cares connected with patents in order to devote his time uninterruptedly to scientific work. Within the past few months he has been appointed Director of the U. S. Bureau of Mines, has been chosen by his colleagues chairman of the Division of Chemistry and Chemical Technology of the National Research Council, and has been presented the Gibbs medal by the Chicago Section of the AMERICAN CHEMICAL SOCIETY.

Warmest possible welcome is given to the first bulletin of the Society of Chemical Industry News Service, of which Dr. E. H. Tripp, Central House, Finsbury Square, London E. C. 2, is Director. This bulletin contains the announcement of the award of the medal of the Society of Chemical Industry to Monsieur Paul Kestner, who "was born in Alsace prior to the German occupation in 1871; he was one of the chief founders and the first president of the Société de Chimie Industrielle in France, which was established in 1917. He has been connected with engineering as applied to chemical industry throughout his career, and among his more notable achievements are the use of forced draught in acid towers, automatic acid elevators, the climbing film evaporator, the scale-less water-tube boiler, and several inventions in connection with beet-sugar manufacture. Very shortly before the armistice M. Kestner gave an address of outstanding interest and importance to the London Section of the Society on 'The Alsace Potash Deposits and Their Economic Significance in Relation to Terms of Peace.' " The problem of public education regarding chemistry is the same in Great Britain as in America. This new medium for distribution of reliable information concerning the British chemical industry will perform a useful public function. We have tried it. We know.

There are those who for reasons easily understood have sought eagerly for justification of complaints about the handling of the reparation dyes by the War Trade Board and the Textile Alliance, Inc. These complainants have willfully ignored the retarding effect of Rhine overflows and the prolonged strike of dock laborers at Rotterdam, and have continually claimed that the British textile industry was getting a jump on the American industry because of tardy methods of our officials. To all such critics it must be somewhat confusing to read in the report of the U. S. Consul General in London (*Commerce Reports*, May 3, 1920, page 677) the following:

> After a long and weary wait the first batch of reparation dyes has been distributed in Yorkshire and has been very heartily welcomed.

But after all—facts are not wanted by those who have axes to grind.

RESPONSIBILITIES OF THE CHEMIST AS A CITIZEN[1]

By H. W. Jordon

Solvay Process Company, Syracuse, N. Y.

Chemists, engineers, and technical men, associated equally with capitalists, have created a new world of industry during the past fifty years, through scientific research applied to the mechanic arts. The automobile, the aëroplane, the submarine, and scores of Jules Verne fairy wonders have grown bit by bit through experimentation into huge, international industries. Our science, applied chemistry, is their foundation. It is not necessary to prove it. It must be admitted. This transformation of the material world has produced intense, breaking stress in the mental world. These industrial changes have brought social conditions which present serious, swiftly growing difficulties. It is our duty to lead in solving the social problems which exist, and helping to direct aright the tendencies of the day, for which we are responsible.

The mental activities, expressed in government, education, and religion, have been stagnant, unresponsive or hostile to the changes in social life. Those to whom we have entrusted government have taken it for granted that methods of administration, drafted for thirteen agricultural, seaboard states in the infancy of the steam engine and forty years before the first railroad, are equally suitable for the engineering age of 1920. Public school education clings to the long summer vacation and the program of the early nineteenth century, when ninety per cent of our people lived on farms where the food, clothing, and all the essential materials of life were grown or manufactured at home. The churches, struggling along with alembic methods in a triple effect age, complain of their declining influence, destroyed by selfish, materialistic city life. To-day seventy per cent of our people live in overcrowded cities, as employees of the industries which arose from our scientific research. Villages and farms have telephones, electric lights, phonographs, and automobiles. Life has been completely reversed, yet we chemists and engineers, prosperous in dollars acquired in creating the causes of world social turmoil, live in the midst of it in indifference. As a civic force, we are ciphers.

NEED OF ACTIVE CITIZENSHIP

First, we should become active citizens, each in his own community. Among civic activities, those relating to modernizing city government, public school education, reform of taxation, reorganization of agriculture, and revivification of the church, are among the most urgent and promising. Many feeble volunteer societies struggle spasmodically with these problems, and attain trifling results. But technical men, immersed in industry, have devoted little time or effort to public affairs. We chemists cannot make social progress by scattered efforts, united only during thirty days before election, against opposing forces of stagnation and reaction that are on the job three hundred and sixty-five days a year.

The entrance of women into government presents a promising force for social improvement. War taught women public work. In peace they have the time to apply their power to reforms, in which they are more practical than men, because they are moved by a deeper sense of idealism. Locally, men can best advance social progress by devoting their personal assistance and resources to support of level-headed, common-sense reforms in government, education, and sociology which women undertake.

Our constructive civic work must be devoted primarily to a new order of city life; to the upbuilding of personal character, through the home, the school and the church; and to what Roosevelt called civic righteousness. Good government of our cities is fundamental to that of the nation. The whole equals the sum of its parts. The character and strength of a nation are the aggregate of its cities, which in turn are the sum of the character of the citizens. Character and the finest qualities of the mind have been smothered in gross materialism. "Never was Carlyle's image of a basket of serpents, each struggling to get its head above the rest, so expressively precise a picture of humanity as it is to-day." The old order of individual selfishness, necessary to self-preservation in the stone age and in colonial days, is impossible in this industrial age. As Samuel Adams said, "Unless we hang together, we will hang separately."

LAW OF MENTAL MASS ACTION

We have evolved the engineering industries by coöperative scientific research. The social world is disintegrating because we have not attempted to build a modern social order by research methods like those through which we created the engineering industries. It has been the notion that man is an individual, free to do what he chooses, and that no laws govern his mental action. But in recent years the combined study of history, statistics, anatomy, psychology and allied sciences, has begun to disclose that man is subject to law as distinct as that of gravity or of chemical reaction. Babson, Carlton Parker, Crile, Cannon, Veblen, and others have shown that mankind acts in mass movements similar to those of the tides; that close relationship exists between the physical body and the action of the mind, and that physical animal life action can exist, entirely dissociated from mentality. These studies indicate that we are at the threshold of a century of mental scientific discovery, succeeding the nineteenth century of disclosure in material applied science.

Had any one in 1820 predicted that within one hundred years man would fly from America to Europe, and that his skill in flying would greatly excel that of the birds, or that with simple instruments he would send messages through the air from Paris to Honolulu, or that he would transmit and accurately reproduce the human voice over a copper wire from New York to San Francisco, a town which did not then exist, he would have been thought in danger of hell-fire, preceded by the fate of the Salem witches.

Sir Oliver Lodge's belief in and hope of development in the mental sphere are conservative, compared with any prophet who, one hundred years ago, might have predicted things as they are to-day.

We are learning that the human mind, in mass action, moving in waves through distinct cycles of years, expresses itself in financial inflation followed by panic, or in war followed by gross speculation and extravagance, which turns into industrial and financial depression and deep distress. Bolshevism, the mania for strikes, desertion of the farms and neglect of agriculture, overcrowding and insufficient housing in the cities, declining birthrate,—all these and scores of similar international wave activities prove man to be almost fluid in his mass response to social law.

The surgical investigators have disclosed that physical degeneration of the brain, the liver, the adrenal, and other glands is coincident with what we had formerly presumed to be purely mental emotions of anger, fright, and worry. As one writer says: "When stocks go down, diabetes goes up." The biologist maintains pulsating life for three months or more by transferring embryo heart tissue of a chick to a suitable culture medium. Sections of veins, arteries, and nerves, dissected from the body and preserved for weeks in alcohol, and then grafted in place of tissue destroyed by accident or in war, begin nerve and blood circulatory functions and ultimately attain normal transfer of blood and nerve action through the alcohol-preserved tissue. These studies prove that human physical and mental life is subject to laws, as definite and as discoverable as those of chemistry or electricity. They await our research.

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[1] Read at a meeting of the Syracuse Section, American Chemical Society, April 30, 1920.

We can no longer expect to attain progress in government and social life by watchfully drifting. We must organize agencies for profound, experimental social research, applied to the mental departments of life. If we do not inaugurate such social research, and maintain it with increasing vigor similar to that of industrial research, our industries, our personal investments, our life insurance, our homes, art, music, and all intellectual and spiritual attainments will be destroyed in political and social chaos, as in Russia. There is chaos because the two wings, the material and the mental, do not flop together. The mental wing is atrophied, and we are headed for a tail spin.

NECESSITY FOR SCIENTIFIC SOCIAL RESEARCH

Eighty per cent of our people lack means of effective public coöperation. Our highest mentality, the graduates of our engineering schools, universities, and colleges, and all intellectual people, have no agency for analyzing and testing their theories of social construction or for registering their opinions in practical, effective public action. Mediocrity is triumphant, because it is organized and aggressively led. In self-defense, we chemists and technical men should establish within our own industries, Departments of Social Public Relations, to educate our own staffs, to study and solve local social problems, and to coöperate with university men and women, with all intellectual people and with the public, in concerted, persistent social progress, based on science.

Next, we should unite our engineering industries with the technical schools and universities, in Federations for Social Research, to undertake the work of evolving the highest attainable individual and national growth in government, education, and religion, by scientific social research. Our fundamental principle should be that of Babson, that action and reaction are equal in the mental world as they are in the physical world; that we get out of life what we put into it. We are getting Bolshevism, class misunderstanding and hatred now, because for the past thirty-five years we have put little else into life than materialism and selfishness. The research would be conducted, under our direction, by engineering schools and universities, through the city, state or national government, to assure authority to our work. Our results would be given full publicity to put the facts before the people, whose judgment is correct if they know the truth. If the truth be frankly and fearlessly presented, there is little need of reform activities. Most abuses are the result of suppression and secrecy.

REVISION OF SOCIAL PUBLIC RELATIONS

Among the possibilities of public service through scientific research are:

(1) There should be reorganization of secondary education. "The war has clearly shown that the popular education of tomorrow must be entirely different from that of to-day," says Anatole France. The Omaha mob which burned the courthouse and nearly lynched the mayor was composed of youths sixteen to twenty-five years old. They committed these crimes "just because they'd nothing else to do." Their school training had been so empty and purposeless that life suggested no other more interesting adventure.

In New York State alone there are about one-half million children who left school at fourteen, and who are employed in ineffective ways in the industries, or more frequently are demoralized through lack of any occupation whatsoever. They are the Omaha mob. Our coöperative organizations of social public relations should develop a plan of citizenship education to combine the resources of agriculture and the industries, in conjunction with the municipal activities of our cities, as the basis of education for this neglected half million. In this age of practical science we have rigidly excluded all children from observation of science applied in agriculture and industry, yet all of us earn our living in these activities. If we would swim, we must get into the water. The city children should be taken on study trips to see the inspiring and interesting phases of life in operation, and become familiar with them. That which they see and observe should be made the basis of broad, liberal education. In this way, we can put daily life and the work of the world back where they were thirty years ago, when the boy and girl got the better part of their education from their daily tasks. Farm and home life in those days compelled growth of observation, attention, and reasoning, and gave us self-reliant Yankees. That was before "Passing the buck" and "Let George do it" were invented.

The training should be designed to make better citizens, and not mere factory operatives. If our people be educated to high ideals of life, if they be raised to high mental and spiritual standards, broad understanding of the interrelation of industries, trade and world commerce, of agriculture and nature, and of the love of books, art and music, they will automatically acquire wholesome home and community interests. If they know the land and its processes, and if they own their homes, they will be good citizens. Few men would fight for a rented flat, but nations have fought for their farms.

(2) Working with the state and federal government we can study to bring about new conditions in the production, distribution, and preparation of food and clothing. We can make individual home ownership and personal thrift a national habit and establish a new social order, adapting the industries and the home to each other. The home and a family of pure racial blood should be the primary motive of our nation, and raising a family should be made more attractive and profitable than its avoidance. We should lay the technical journals on the shelf for awhile and read Madison Grant's "The Passing of the Great Race," and Lothrop Stoddard's "The Rising Tide of Color."

(3) Industry in recent years has been the victim of lack of truthful publicity. In conjunction with the universities and other agencies representing highest national intellectuality, we should present the truth through the press, so that the public may realize that our research is solving the baffling and complex problems of social life. The packers and milk distributors are spending money lavishly to put the truth in the minds of the people by explanatory advertising, one to ten years belated. If we are sincere, we can secure coöperation of great journals, daily, weekly, and monthly, and through them place our work before the nation in a manner so convincing that it will insure our ultimate, complete success. Truth and publicity are absolutely destructive to social abuses. The evil results of venereal disease are being steadily diminished by frank, dignified publicity. We need to study the problem of "Liberty and the News," as analyzed by Walter Lippman in his recent book of that title.

(4) We should develop a new class of engineers trained at the technical schools and universities to occupy positions in city, state, and national government similar to those occupied by engineers in industry. Their work should assure a lifelong career, with tenure of office based on merit, and transfer or promotion free from political, partisan, or sectarian influence. They should be the men who execute and maintain the findings of our social research. Through these engineers of social technology, we would rescue government from corroding reaction and put it on a modern basis of progressive, applied engineering. We would substitute scientific economics for the existing order of government by selfish, unenlightened, partisan politics.

The work proposed, though apparently highly idealistic, is merely the self-preservation of business and social life from the dangers of swiftly progressive mediocrity. The four examples cited are only a few of the possibilities of social scientific research, attainable by a federation of the chemical and engineering industries, working in conjunction with the engineering schools and universities through the authority of city, state, or national government. A nucleus already exists in the National Research Council, which includes departments of medical sciences, of biology and agriculture, and of anthropology and psychology. We should quickly expand that work by undertaking the most urgent tasks of social research in several industrial cities.

The object sought has been well described by Professor George F. Swain: "Continued progress and the interest of the social organism as a whole require that individual initiative and ability shall be encouraged to the utmost and allowed to enjoy the reasonable fruits of its exercise; that property should be protected; that taxation shall be equable and uniform; that leaders shall be chosen from those most capable and judicious; and that those who are only fitted for manual labor shall not acquire a distaste for it or look down upon it as inferior in dignity to other occupations; that waste and extravagance shall be reduced to a minimum."

AGRICULTURAL *vs.* INDUSTRIAL EPOCH

As an illustration of the splendid possibilities of scientific social research, let us outline a research study of agriculture in conjunction with education. The United States is a powerful, unique nation. Our close contact with nature, the sea and the wilderness, and the individual ownership of our farms and homes, made us intensely independent and highly individualistic. Each one was free to develop his ability within his natural limitations, in a country of vast resources. Coincident with exhaustion of the free land, we entered the industrial era and our population shifted from 80 per cent agricultural to 70 per cent city dwelling, and a vast influx of Slavs, Semetics, Latins, Southeastern Europeans and Western Asiatics diluted our English and Northern European stock to a minority. Thus we have land and racial problems, in addition to those of congested city industrialism.

Formerly the child learned life by living. The household arts which used to supply home technical training have been almost completely superseded by factory manufactured food and clothing. Our light and fuel for cooking are delivered to our homes through pipes or over wires, displacing the kerosene lamp and the wood pile, the old oaken bucket and the chain pump, and the bucksaw. The water wheel at the brook, the wind wheel on the woodshed, the figure-four trap and the muzzle loading shotgun have been supplanted by Mary Pickford, Douglas Fairbanks, and Charlie Chaplin, witnessed seated, in a dark room. Healthful play at home is rarely possible, for there is neither room nor play space. Play is transferred to city parks, where unmarried women of advanced years are hired to *teach* children to play.

The schools of former days and the long summer vacation were designed for New England village and farm life. The red schoolhouse education of that time was adequate, because the training in practical life which children received from their daily work at home produced self-reliant Yankees. The industrial changes during the past thirty-five years have robbed children of active experience in life, and have given them passive, commercialized amusement instead. Migration from the farms is making us a restless, discontented, purposeless nation, flabby in muscle and in mind. We are being transformed from red-blooded, rigid vertebrates, to water-white, sloppy, physical and mental mollusks, encased in a shell of organized labor.

With this topsy-turvy condition in education, there came similar inversion in farm life and food production, aggravated by unenlightened and wasteful methods of food distribution. And finally we have entered upon a deplorable decline in the influence of religion. The religious spirit, based upon close touch with nature and ownership of the land, degenerates and dies when a nation falls under the control of commercialism or industrialism. The people leave the farms they own and become city tenants. They flock to Babylon, Athens, Rome, New York, where they succumb to unimaginative materialism. They lose their love and fear of nature, their respect for law and authority, and their reverence for the Deity. They no longer have chivalrous regard for womanhood. Marriage, the home, and the family cease to be the prime motives in life, the pursuit of pleasure and luxury becomes dominant, and there is general subsidence in art, music, and the finer qualities of the mind. Spiritual indifference follows, ending in the decline and death of religion.

FIELD FOR SOCIAL EXPERIMENTATION

One of our most urgent social tasks, perhaps the most urgent, is scientific social research upon the interrelation of agriculture and country life, and the industries and city life in their practical bearing upon education and religion. Therefore, let us conduct a social experiment to give our city boys some measure of American education by contact with nature and the land, like that which our sturdy Yankee grandfathers received.

An experimental group of boys, about one hundred, of ages eighteen, nineteen, and twenty, would be assembled and assigned to farm life combined with school training. The periods would be for the farm growing season of seven months, April to October, inclusive, of their eighteenth and nineteenth years, and for the entire time of their twentieth year of age. The boys would be quartered in a suitable cantonment, in the center of a typical farm district to do the work on the farms, as many of our older chemists did when they were boys. They would be paid as we were, by their board, clothes and education, with some, preferably a small amount of, spending money.

Associated with their work, these boys would be given a generous amount of education in agriculture by simple, interesting, scientific instruction through lectures, farm and field demonstrations, and moving pictures. The fundamental principles of raising crops, preparation of the land, selection of seed, production and use of fertilizers and care of the crops from sowing to harvest should be taught, as well as the storage of the crops and their distribution to market. The breeding of poultry, cattle and all live stock should be taught, with special emphasis laid on the economic importance of pure breeds and the selection of the most productive individuals for breeding, as proved by the experience of Holstein-Friesian breeding for milk production. Good breeding pays, whether of Holsteins, hogs or humans.

There would be abundant opportunity to teach many scientific facts of the out-of-doors relating to production of fruit and garden vegetables, protection against insect pests, cultivation of flowers and practical forestry. A multitude of interesting topics regarding nature would occur to any alert teacher.

This instruction would afford not only pleasing recreation from manual labor, but also would give our boys broad and liberal education in agriculture and nature, and create an interest which would attract many of them permanently to the farm. It would give all of them robust health and keen, lifelong interest in out-of-door life, and bring them into educational balance with the other ten per cent of high school boys. The educational portion of the experiment could be in charge of the state agricultural college.

The abundant supply of dependable labor from this source would permit farm work to be done in two shifts of six or eight hours, covering the entire day from sunrise to sunset. This arrangement of shifts would remove all cause for objection by the farmer to daylight saving, because he could direct his work to best advantage at all hours of the day.

As the boys would be in excellent condition from not more than eight hours' labor, they could multiply the production of the farms by thorough, intense cultivation. Wasteful use of land could be ended. Inferior pasture or bush land could be brought into fruitful production or planted as forests. Rich bog lands could be drained. Scrub growth corners could be made permanent forests. Roadsides could be beautified and used for pasturage and fruit. Sheep-raising could be promoted to fertilize abandoned farms and to produce mutton and wool.

A further advantage would be that tractors could be used intensely, by sending them from farm to farm and keeping them in action sixteen hours a day. In the rush season, tractors drawing plows or harrows could be used twenty-four hours a day, with the help of artificial light supplied by the tractor engine, and operated by eight-hour shift labor.

Housing the boys in central camps would relieve the farmer's wife of the drudgery she now endures during the growing season, and would interfere in no way with the home life of the farmer. The boys could be trained in the Swiss military system, if desired. A steady hand and keen eye would be developed by competitive rifle marksmanship.

REDUCTION OF "H. C. L." ASSURED

Three great fundamentals of living are food, clothing, and housing. Food is the product of agriculture. Wool, cotton, leather, and linen, the raw materials of clothing, are products of agriculture. Lumber, an important material in housing and in furniture, is a product of forestry, which is tree agriculture. The high cost of living can be reduced by abundant, cheap production of food, clothing, and housing. That result can be assured if this system of coöperation between education and agriculture be evolved and brought into general practice, as the result of our scientific research.

The most highly perfected social organization in the world is that of the bees, who produce not only sufficient food for themselves but a liberal surplus for export to mankind, by their thoroughly organized food production. The plan proposed is essentially identical with that of the bees.

Country life compels attention, observation, reasoning, foresight, self-reliance and sturdy health. The Elkhorn ranch transformed Roosevelt from a sickly youth to our best example of vigorous physical and mental American life; and boyhood on the farm was the basis upon which Lincoln and most of the great American mental leaders built their lives.

The trends of civilization are swiftly flowing into a vortex of highly socialized life, directed by government. And government is becoming an aggregate of applied science through engineering. The situation is analogous to that in industry when Cornell, the Massachusetts Institute of Technology, and other engineering schools, were founded to educate engineers of applied material science as directors of industry. An extraordinary opportunity and duty confronts us: that we build a new social, intellectual, and spiritual structure, commensurate with our material one. For, as Anatole France recently said: "Whether we like it or not, the hour is at hand in which we must choose between being citizens of the world, or spectators at the death of civilization."

CHEMICAL INDUSTRIES AND TRADE OF NORWAY

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Norway is a thinly populated country with only a few notable natural resources, chief of which are the forests, fisheries, and water power. Of minerals, iron ore and cuprous pyrites are the only items that need be considered. Not more than 3 per cent of the area of the country is under cultivation, and it is estimated that fully three-fourths of that area are absolutely unsuited for agricultural development. Another serious handicap is the lack of native coal.

There has been, however, a great accumulation of wealth as a result of the war, for timber, fish, and electrochemicals have been exported in large quantities at very advantageous prices, and Norwegian shipping, in spite of all vicissitudes, has earned splendid dividends. This wealth will be used to develop native industries and will be put into hydroelectric projects, into the development of a real iron and steel industry, and into agriculture. Before the war Norway had been exporting a few dairy products, but importing cattle feed and cereals, and the disadvantages of such an arrangement have been amply demonstrated during the last few years. Much of the wealth will naturally be spent outside of the country for equipment for the new developments and for a long list of necessities and luxuries that were difficult to obtain during the war. The American chemical industry will be interested in the extent to which the manufacture of electrochemicals is to be developed and in the extent to which dependence will be placed upon outside sources for other chemical products.

ELECTROCHEMICAL INDUSTRIES

It is estimated that the water power available in Norway is not less than 15,000,000 horse power, of which about 1,500,000 horse power are now actually utilized. It is widely distributed and, in the absence of coal, electricity is commonly used to an extent and for a variety of purposes that would be surprising even to an American. The greatest development has been along electrochemical lines, but there is an increasing call for current in the metallurgical industries, and it is used liberally for power, lighting, and heating.

Calcium carbide was the first product of the Norwegian electrochemical industry and production was so greatly stimulated by the war that the capacity has been wonderfully developed. The total output in 1915 was estimated at 100,000 tons, but large plants have been erected since that time. In that year one concern produced 60,000 tons and another 30,000 tons. A considerable proportion of the carbide is now used in the manufacture of cyanamide.

As every chemist knows, it was cheap Norwegian electricity that made possible the first commercial utilization of atmospheric nitrogen. Between 300,000 and 400,000 horse power are now used in Norway for the production of nitric acid, calcium nitrate (commonly known as "Norwegian saltpeter"), and other nitrates and nitrites. The future of this industry is considered very promising.

There was a time when a great deal of iron was smelted in Norway from the native ores, but even before the war this industry was declining with the rise in the price of coal, and after hostilities began most of the remaining plants were obliged to close. Much attention is therefore being given to the establishment of electric-smelting plants and there seems to be a good future in that direction. One plant that was in operation when the war began found it very difficult to obtain electrodes, but these are now manufactured in the country. Plans are under way for the development of an electric steel industry in connection with the smelters.

Electricity is also used in the production of aluminum, much of which is used in connection with air-nitrate plants, and in the manufacture of ferrosilicon. A good idea of the character and quantity of articles produced electrolytically can be obtained by studying the table of exports in this article.

IMPORTANCE OF FISHERIES

In value, the exports of fish and fish products amount to about half of the goods shipped out of the country. Cod, herring, whale, mackerel, and salmon form the principal catches, and the by-products of the industry are of interest to the chemist. Great quantities of oil are obtained from the livers of the cod, while the heads are used for fodder and fertilizer. Oil is also obtained from the blubber of the whale, the bones are crushed for use as fertilizer, and the flesh is used for both fodder and fertilizer.

OTHER CHEMICAL INDUSTRIES

As in Sweden, the production of wood pulp has grown to striking proportions in Norway, and the manufacture of paper has become increasingly important. Exports of pulp amounted to nearly 700,000 tons in 1913, the greater part going to England. Import restrictions in various countries and difficulties in shipping decreased the sales abroad, but the general demand since peace was declared bids fair to continue and means renewed prosperity to the Norwegian manufacturers.

Oxalic acid is made from sawdust and is an important item of export, the United States being one of the best customers.

Matches also go into the export trade in large quantities, although the industry has not reached the proportions attained in Sweden.

With supplies of native apatite, the manufacture of superphosphate has been developed to the point where more than 50,000 tons can be produced annually, as compared with a pre-war production of 20,000 tons.

Before the war, Norway imported something like 1,400,000 lbs. of soap of various kinds, a large quantity when the small population is considered. As there is a scarcity of oils suitable for the manufacture of soap, it is likely that a good market will continue for imported soap. Before the war, England supplied the demand to a large extent, but during the last few years American manufacturers have been doing about 40 per cent of the business and their products are enjoying popular favor.

STATISTICS OF PRODUCTION

There are no figures available to show the quantity and value of the production of chemicals and allied products in Norway, but the following table will serve to show the effect of the early years of the war upon such industries. It has been compiled from official returns issued by the Government Bureau of Insurance:

Some Effects of the War upon the Chemical Industries

	1913			1917		
Industries	Factories	Operatives	Average daily wage. Dollars	Factories	Operatives	Average wage per hour. Cents
Bone grinding	2	7	1.09	2	5	15.3
Calcium carbide	5	1,063	1.40	4	1,654	24.4
Candles	1	27	1.07	1	14	25.7
Cement	1	297	1.37	4	404	24.4
Chemicals:						
Heavy	7	219	1.15	11	381	24.4
Minor	27	137	1.00	32	243	18.8
Colors	10	73	1.09	13	162	19.0
Electrochemicals	12	2,497	1.50	12	4,847	31.9
Explosives	7	268	1.16	8	570	21.7
Fertilizers	14	140	0.82	15	106	18.0
Gas works	11	143	1.03	9	87	19.8
Glass	12	1,064	1.21	16	864	18.0
Glue	5	75	0.92	6	95	16.3
Insulating materials	5	28	1.29	3	58	16.9
Matches	4	919	1.29	4	928	20.4
Oils and by-products	42	663	1.02	51	907	22.0
Paper and cardboard	42	4,920	1.13	47	5,390	18.5
Perfumes	1	8	0.64	1	5	20.4
Pharmaceuticals	12	76	0.77	12	92	19.6
Refining oil	6	256	1.16	6	426	21.2
Refining petroleum				1	69	22.5
Soap	19	116	0.98	17	109	18.8
Soap, candles, perfumes	13	205	1.00	12	265	16.6
Tanneries	78	574	1.03	83	736	20.4
Tar paper	5	25	1.00	9	52	20.9
Train oil	78	360	0.91	82	295	18.8
Treatment of ores	11	617	1.25	17	1,455	30.6
Varnishes	6	41	0.98	6	42	23.3
Wood pulp:						
Chemical	27	5,261	1.17	27	5,099	20.9
Mechanical	69	3,735	1.03	67	3,010	17.4

As Norway is seeking to equip herself to refine and work her own minerals, the following table is inserted to show the materials available. The statistics are issued by the Norwegian Bureau of Statistics.

Production of Minerals

Minerals	1913 Metric Tons	1915 Metric Tons	1916 Metric Tons
Silver and silver-bearing ores	5,411	8,431	7,515
Copper ores	70,349	56,097	28,670
Pyrites (iron and copper)	441,291	513,335	295,354
Nickel ore	49,990	77,018	79,903
Iron ore	544,686	714,917	417,899
Zinc and lead ores	897	1,829	1,017
Chrome ore	.....	350	2,757
Molybdenite and wolfram	12	97	137
Rutile	77	170	103
Bismuth ore	.....	10	.....
Graphite	300	.....	.....
Apatite	757	1,901	2,236
Feldspar	40,842	8,778	12,811
Other	1,500	380	5,640
Total	1,156,112	1,383,313	854,042
Total Value	$5,753,500	$11,020,400	$8,227,900

THE MARKET FOR IMPORTED CHEMICALS

As already shown, Norway is displaying great activity along certain chemical lines, but it should be borne in mind that the variety of products is decidedly limited and that almost total dependence is placed upon outside sources for the bulk of the articles usually described as chemicals and allied products. In some of these lines American manufacturers have successfully entered the market since the war started and their wares have made a uniformly good impression. The character and extent of the requirements of the market can be determined by a study of the following table, which is based upon official figures published by the Norwegian Central Bureau of Statistics:

IMPORTS OF CHEMICALS AND ALLIED PRODUCTS

	1913 Pounds	1916 Pounds	1917 Pounds
CHEMICALS, DRUGS, DYES, MEDICINES:			
Acids:			
Boric	23,869	40,816	41,010
Carbolic, pure	15,084	32,222	23,215
Carbonic, liquid	4,328	13,827	882
Citric and tartaric	34,535	104,824	49,653
Muriatic	604,200	546,265	604,364
Nitric	61,632	386	.....
Sulfuric	6,473,698	3,239,748	1,555,427
Germany	1,128,712	649,189	1,940
Netherlands	3,879,346	.....	.....
Sweden	1,390,133	2,567,256	1,539,532
United Kingdom	176	15,322	2,756
United States	.....	.....	10,648
Other acids	175,532	338,488	365,187
Alum	6,886,796	7,001,413	3,762,519
Germany	.....	135,473	250,578
Sweden	.....	2,700,150	1,774,809
United Kingdom	.....	3,082,670	796,354
United States	.....	1,083,120	940,778
Ferric	(1)	408,918	773,485
Ammonia, anhydrous	(2)	35,171,042	18,327,136
Ammonia compounds: salt of hartshorn	232,830	467,671	264,246
Other	.....	4,431	3,217
Baking powder	30,875	38,331	27,935
Bromides, iodides, and cyanides of metals	(1)	68,112	6,484
Bromine	.....	.....	70
Camphor	11,380	10,523	21,332
Carbon disulfide	.....	8,437	12,216
Casein	31,557	10,335	10,692
Chemicals, n. e. s	238,333	888,520	104,608
Chloride of lime	7,418,788	5,169,590	2,339,568
United Kingdom	.....	2,282,488	.....
United States	.....	2,584,496	2,132,553
Chlorides of metals, n. e. s	(1)	57,494	6,371
Drugs, n. e. s	1,350,547	1,613,540	1,284,386
Dyes and dyestuffs:			
Aniline and alizarin dyes	669,985	633,192	789,319
Germany	532,700	577,191	766,402
Netherlands	119,386	822	.....
Switzerland	441	10,198	.....
United Kingdom	635	11,041	.....
United States	.....	18,631	805
Chemicals, herbs, roots, etc., used in dyeing	225,908	83,224	109,724
Cochineal	2,987	126	.....
Dyewood extracts	206,536	454,787	1,325,637
Indigo	12,493	4,266	6,665
Germany	8,670	4,156	6,665
Explosives:			
Gunpowder, smokeless, including ballistite	1,243	17,884	.....
Other; dynamite and other explosives	133,092	719,493	205,851
Fireworks	21,449	17,008	19,361
Matches of wax, stearin, etc	(1)	24	.....
Other	(1)	3,988	6,890
Miners' fuses	112,590	109,225	262,172
Friction tinder boxes	(1)	24	55
Glycerol	941,306	1,262,378	324,628
Germany	216,449	.....	.....
Netherlands	380,163	936,157	225,535
Sweden	.....	111,945	54,077
United Kingdom	328,672	211,921	45,012
Glycerol dip	2,116	3,307	.....
Hydroxides, n. e. s	(1)	8,792	23,391
Insect powder	60,803	92,022	115,020
Magnesium chloride	(1)	700,785	992,907
Oxides, n. e. s	(1)	743,018	202,580
Oxygen	9,694	710	134
Perfumery and cosmetics:			
Creams and paste, solid or liquid	24,230	16,034	11,041
Fumigating materials	37	.....	342
Hair oil	2,050	1,669	2,560
Pomatums and cosmetics	18,371	28,911	26,118
Toilet waters, alcoholic	20,161	32,262	32,132
Non-alcoholic	1,775	12,110	9,156
Phosphate of lime (for cattle feed)	462,133	77,18	560,415
Phosphorus	67,251	73,753	40,977
Potash	1,262,089	2,128,410	1,238,976
Germany	953,842	1,910,418	835,993
Sweden	154	32,584	11,354
United Kingdom	300,796	131,990	.....
United States	.....	53,418	391,430
Caustic; potash lye	2,472,350	3,237,252	2,688,510
Potassium chlorate	820,552	2,139,720	23,589
Chloride	(1)	1,118,434	701,692
Nitrate	1,151,771	20,811	.....
Germany	1,133,606	.....	.....
United Kingdom	12,059	.....	.....
United States	.....	20,811	.....
Rat poison	10,538	7,987	12,762
Rennet; cheese coloring	85,165	92,096	75,923
Salt prepared for medical use	34,917	7,030	1,296
Salts of metals, n. e. s	(1)	6,806	1,120
CHEMICALS, DRUGS, ETC. (*Concluded*):			
Soda, calcined	36,161,414	57,011,948	61,174,100
Austria-Hungary	.....	8,158,321	.....
Belgium	11,454,109	.....	.....
France	21,826	3,322,552	10,999,125
Germany	19,458,041	8,538,107	76,390
Sweden	52,161	228,529	15,630
United Kingdom	5,108,058	36,341,751	43,455,460
United States	.....	359,703	6,627,495
Caustic	3,790,848	4,861,575	3,969,600
Germany	.....	854,000	356,002
United Kingdom	.....	2,968,610	742,025
United States	.....	920,900	2,865,257
Sodium biborate	237;288	1,380,540	304,026
Bicarbonate	325,930	437,591	189,487
Sulfate	24,803,470	28,490,575	13,244,467
Sulfite and other salts	2,296,504	635,196	838,970
Soluble glass	954,548	966,893	878,807
Sulfates of copper, iron, zinc	381,513	1,075,670	490,297
Sulfates of metals, n. e. s	(1)	509,014	480,449
Sulfur	33,974,910	16,010,650	8,974,180
Italy	16,307,327	8,627,745	2,183,280
Spain	4,288,144	540,132	.....
United Kingdom	12,016,360	6,734,438	335,014
United States	.....	108,335	6,455,862
Tanning materials:			
Barks and extracts	13,333,796	13,677,670	8,048,239
Argentina	.....	3,611,157	2,614,902
South America, other	.....	1,831,361	.....
East Africa	.....	2,088,043	595,468
France	585,343	5,776	8,818
Germany	7,292,311	23,214	.....
Russia	2,098,382	110,230	478,403
Sweden	1,123,420	399,100	1,208,860
United Kingdom	1,337,266	2,709,520	765,379
United States	51,257	1,960,242	309,440
Catechu and gambier	532,786	1,876,556	638,900
Divi-divi	589,201	631,717	248,108
Gallnuts and valonia	88	.....	.....
Tartar	37,192	75,532	44,033
Tin salts	875	33	159
Fertilizers:			
Ammonium sulfate and other salts	19,839,740	16,677,323	21,452,700
Sodium nitrate	2,948,211	14,166,208	98,757
Cyanamide	.....	10,653,705	7,272,168
Kainite and other potash salts	46,541,553	26,123,121	25,138,310
Germany	46,138,800	22,781,388	25,138,310
Portugal and Madeira	.....	2,909,852	.....
Sweden	.....	420,858	.....
Superphosphates	9,683,860	24,566,960	82,524,595
France	.....	756,178	.....
Portugal and Madeira	.....	23,810,716	.....
United States	.....	.....	73,555,080
Thomas phosphate	76,622,686	18,414.792	.....
Portugal and Madeira	.....	4,589,803	.....
United Kingdom	18,726,393	13,636,934	.....
Belgium	38,455,625	.....	.....
Other fertilizers	4,011,093	711,138	887,735
PAINTS, PIGMENTS, COLORS, VARNISHES:			
Black: bone black, lampblack, graphite, pot-lead	1,065,074	972,459	1,163,512
Blacking, shoe and stove polish, leather creams	281,691	293,205	254,934
Chalk, ground; baryta, china clay	32.138,497	37,580,367	17,678,007
Denmark	.....	.....	8,678,011
Germany	.....	.....	3,464,211
Sweden	.....	.....	3,912,015
United Kingdom	.....	.....	309,595
Ink, liquid	89,851	63,107	53,852
Powder; India ink	4,588	8,896	7,915
Printers', of all kinds	312,226	279,933	108,855
Lead, red	992,665	1,253,756	583,564
White	193,013	177,735	230,163
Ocher, amber, English red	3,877,578	3,337,930	2,730,160
Paint boxes; paints in tubes, vases	26,468	33,860	33,014
Paints ground in oil	206,617	288,760	194,205
Compounded with tar, including paint for ships' bottoms	299.762	396,453	330,274
Germany	.....	62,280	2,183
United Kingdom	.....	313,032	325,579
United States	.....	2,227	375
Paints, liquid, n. e. s	67,941	22,754	33,107
Mixed, in packets	34,586	78,484	29,723
Sugar coloring for brandy	8,768	.....	3,241
Varnishes containing alcohol	52,714	37,716	11,360
Other	820,949	585,520	454,902
Zinc white and dutiable dry paint	5,322,213	5,990,998	5,514,162
Belgium	280,271	11,486	.....
Germany	3,576,126	5,576,076	4,436,547
Netherlands	1,370,907	214,773	12,932
Sweden	7,121	34,577	1,016,765
United States	110	8,516	33,676
SOAP AND CANDLES:			
Candles, stearin and tallow	69,685	9,015	60
Wax	6,537	1,327	1,043
Soap, green; unscented soap powder	119,981	70,946	94,545
Sweden	85,212	12,588	.....
United Kingdom	13,754	53,492	72,298
United States	4,978	4,729	21,890
Transparent, or perfumed	87,476	105,340	181,273
Germany	38,773	1,294	240
United Kingdom	35,078	70,437	134,634
United States	2,293	18,585	36,980

[1] Not shown separately.

[2] Under "fertilizer" in 1913.

IMPORTS OF CHEMICALS AND ALLIED PRODUCTS (*Continued*)

	1913 Pounds	1916 Pounds	1917 Pounds
SOAP AND CANDLES (*Concluded*):			
Other	1,358,590	1,024,967	2,645,027
Germany	29,160	.....	.....
United Kingdom	1,296,373	891,761	1,442,467
United States	3,997	125,391	1,198,012
OILSEEDS:			
Copra	9,711,714	17,239,044	10,939,250
Linseed	32,510,186	27,542,437	13,385,652
Argentina	17,219,290	11,438,926	11,461,633
South America, other	5,070,741	.....	.....
British India	.....	7,009,795	1,922,430
Russia	4,791,526	.....	.....
United States	2,889,245	5,643,370	.....
Rapeseed	2,124,572	236,800	655,125
Belgium	2,003,318	.....	.....
British India	.....	.....	651,774
United Kingdom	.....	236,337	.....
OILS, FATS AND WAXES:			
Fatty oils:			
Butter coloring	41,048	73,940	57,609
Castor oil, resin oil, and other fatty oils, n. e. s	7,314,694	4,255,075	14,358,088
Denmark	410,369	51,080	9,155,312
France	934,981	1,527,230	1,672,559
Germany	2,963,850	.....	.....
Netherlands	2,341,176	674,085	57,232
United Kingdom	182,388	640,928	3,064,668
United States	302,253	1,319,290	394,760
Coconut oil	8,016,866	5,974,902	2,182,069
Asia, n. e. s	.....	1,937,950	1,755,760
British India	5,002,177	1,865,110	.....
France	453,403	547,562	265,965
Germany	1,208,022	.....	.....
United States	93,652	339,798	32,870
Corn oil	30,336	76,787	.....
Cottonseed oil	11,563,817	23,680,157	27,433,308
Brazil	.....	9,634	356,046
Germany	572,981	.....	.....
Netherlands	2,383,611	304,567	.....
United Kingdom	1,572,182	564,736	59,304
United States	6,842,860	22,744,493	26,557,742
Hempseed oil	31,570	3,042	31,195
Linseed oil, raw	1,409,547	1,446,717	2,830,360
Boiled	1,918,109	851,270	1,262,345
Netherlands	497,407	73,193	159,593
United Kingdom	1,399,494	762,910	336,557
United States	.....	11,640	766,195
Olive oil	2,408,439	7,392,606	3,863,050
France	1,011,878	239,576	71,496
Italy	701,643	48,060	2,072
Spain	569,873	7,080,167	3,723,300
Palm oil	174,341	107,740	211,357
Rapeseed oil	482,592	210,078	195,991
Sperm oil, olein, lard oil	578,934	340,702	1,234,897
Belgium	65,323	.....	.....
Germany	128,816	.....	.....
Netherlands	301,482	18,342	.....
United Kingdom	38,251	257,853	825,036
United States	.....	35,120	323,572
Whale oil, cod liver oil, fish oil	4,607,727	3,301,245	7,720,124
Linseed oil, raw; rapeseed oil, palm oil	2,066,480	1,764,535	3,237,710
Germany	528,823	882	.....
Netherlands	539,714	1,587	523,664
United Kingdom	794,965	1,568,875	910,818
United States	375	40,300	1,803,228
Volatile oils:			
Turpentine, juniper, birch oils	362,833	597,667	298,528
Other	25,693	33,272	32,392
Blubber, cod liver, etc	.....	13,073	992
Lye of fat or train oil; degras	937,560	218,720	181,396
Stearin, palmitin, paraffin, spermaceti	1,628,670	4,553,665	1,372,964
Germany	499,305	82,487	.....
Netherlands	273,635	56,720	.....
United Kingdom	759,374	3,648,858	642,564
United States	3,770	743,554	729,706
Tallow, oleomargarine and other greases	18,237,497	26,127,486	24,843,734
Argentina	227,054	3,010,985	3,846,603
Germany	2,357,270	2,359	1,124
Netherlands	1,357,562	327,739	.....
United Kingdom	2,410,666	2,252,838	349,100
United States	8,730,040	19,895,196	18,259,542
Wax	82,500	740,826	85,504
ORES:	Metric tons	Metric tons	Metric tons
Aluminum oxide, bauxite, cryolite	4,363	12,071	10,291
Chrome ore	.....	2,897	4,677
Nickel ore	569	.....	.....
Pyrite	.....	600	.....
Pyrite slag	.....	323	.....
Zinc ore	.....	.....	330
VARIOUS PRODUCTS:	Pounds	Pounds	Pounds
Glass	9,766,930	13,984,685	29,613,365
Glue:			
Capsules of gelatin, filled	505	258	298
Isinglass and gelatin in sheets	37,811	31,561	10,880
Liquid glue, etc	43,930	38,620	32,205
Other	492,450	438,973	475,920
Sizing	643,443	459,880	220,855
Paper, except printed matter	18,058,300	25,054,937	31,267,910
Pitch and coal pitch	1,463,160	3,078,050	1,664,755
Tar:			
Coal tar	2,210,905	1,857,504	871,245

IMPORTS OF CHEMICALS AND ALLIED PRODUCTS (*Concluded*)

	1913 Pounds	1916 Pounds	1917 Pounds
VARIOUS PRODUCTS (*Concluded*):			
Tar (*Concluded*):			
Wood and peat tar	4,124,320	5,848,775	2,449,200
Creosote, creosote oil, raw phenol	5,511,620	3,222,894	1,961,188
Turpentine	1,373	1,204	3,461
Rosin and similar gums	8,103,970	11,074,500	2,053,958
Woodpulp, straw pulp	69,132	91,853	54,103

EXPORT TRADE

The extent to which the Norwegian chemical industries have exceeded the needs of the home market in certain specialties is made evident in the next table, compiled from figures published by the Central Bureau of Statistics:

EXPORTS OF CHEMICALS AND ALLIED PRODUCTS

	1913 Pounds	1916 Pounds	1917 Pounds
CHEMICALS:			
Acids:			
Caprylic	120,364	4,493	.....
Carbonic	.....	4,980	.....
Nitric	4,630	8,887,340	3,575,170
Oxalic	1,220,030	960,505	736,533
France	.....	278,590	97,074
Japan	.....	139,255	148,428
United Kingdom	134,938	29,388	237,597
United States	1,026,638	379,955	170,089
Sulfuric	507	.....	611,531
Aluminum sulfate	.....	66,216	688,082
Ammonium nitrate	20,078,315	131,481,474	140,165,745
France	.....	74,249,430	102,418,975
Russia	.....	36,815,515	15,300,784
United Kingdom	.....	16,926,780	21,390,790
United States	.....	1,427,427	156,815
Calcium carbide	147,513,146	128,822,470	101,559,524
Australia	29,473,568	7,569,680	782,860
Denmark	1,414,574	2,421,072	8,136,687
Germany	46,023,063	63,952,370	53,763,924
Netherlands	4,903,190	4,320,290	2,249,640
United Kingdom	21,715,543	39,969,690	34,912,727
Casein	249,160	132,487	305,160
Drugs, n. e. s	1,603	12,075	2,046
Explosives:			
Gunpowder and other explosives	38,228	32,337	2,491
Dynamite	4,253	1,292	.....
	Metric tons	Metric tons	Metric tons
Fertilizers:			
Ammonium sulfate	138	.....	50
Cyanamide	22,111	13,152	2,313
Germany	12,188	.....	.....
Netherlands	1,591	1,253	.....
United Kingdom	3,444	10,172	1,320
Norway saltpeter	70,927	46,001	35,932
Denmark	4,512	.....	1,118
France	8,738	1	.....
Germany	45,238	19,805	16,279
Sweden	139	1,130	1,425
United Kingdom	4,874	25,062	17,110
	Pounds	Pounds	Pounds
Glycerol, raw	277,483	309,756	66,615
Iodine, raw	26,784	2,493	2,601
Magnesite, calcined	1,446,232	3,673,120	1,054,603
Matches	12,106,628	11,331,030	8,916,990
British India	3,498,736	1,374,030	965,404
Russia	5,790	4,409,840	2,946,940
United Kingdom	3,467,870	3,405,237	185,607
United States	2,291,264	1,494,293	3,579,579
Nickel sulfate	.....	11,043	.....
Oxygen	.....	.....	3,142
Phosphorus	.....	.....	37,285
Potassium chlorate	.....	628,364	.....
Rat poison	.....	11,840	17,857
Salt of lemons (bioxalate of potassium)	90,072	62,333	64,534
Silicon carbide, durubit, etc	3,638	2,196,355	1,485,520
Russia	.....	457,690	76,170
Sweden	.....	1,534,395	1,122,946
United Kingdom	.....	44,820	211,798
Soda crystals (washing soda)	1,262,080	905,900	.....
Sodium bisulfate	3,760,149	551,156	.....
Chlorate	.....	27,550	174,665
Nitrate	2,483,000	32,590,820	50,069,622
France	.....	.....	5,236,573
Sweden	.....	2,969,956	2,300,413
United Kingdom	.....	29,143,233	42,498,947
United States	.....	170,615	.....
Nitrinitrate	4,448,910	14,198	.....
Nitrite	18,085,920	13,468,633	7,795,743
Germany	2,829,774	6,806,154	662,864
Netherlands	13,561,570	65,852	15,917
United Kingdom	699,313	3,295,360	5,774,347
United States	721,273	3,054,813	1,196,338
Peroxide	(1)	53,694	48,127
Soluble glass	202,023	34,260	.....
Tanning materials:			
Oak bark	114,640	836,826	.....
Other barks	24,612	27,370	.....

(1) Not shown separately.

EXPORTS OF CHEMICALS AND ALLIED PRODUCTS (*Continued*)

	1913 Pounds	1916 Pounds	1917 Pounds
PAINTS, PIGMENTS, ETC.:			
Copper paints for ships' bottoms	527,068	28,984	.....
Paints ground in oil	25,850	67,228	23,931
Zinc white and white lead	106	676,334	354,944
Other paints and colors	75,422	1,453	1,576
Varnishes	46	538	.....
OILS, FATS AND WAXES:			
Coconut oil	(1)	2,119,720	.....
Linseed oil, rapeseed oil	25,413	10,211	606
Train oil, gallons	7,086,670	5,397,964	1,003,690
Austria-Hungary	44,804	128,232	.....
Germany	3,574,378	3,230,420	585,708
Netherlands	931,411	7,582	238
Russia	56,323	90,428	206,323
United Kingdom	813,826	878,681	115,763
United States	260,664	81,552	78,038
Turpentine oil	.....	.....	19,758
Vegetable oils, solid	53,215	690,190	.....
Bone fat	535,975	660,152	191,780
Blubber	53,398	8,201	.....
Stearin, gallons	175,600	24,991	14,054
Germany	100,335	23,961	3,963
Sweden	18,149	53	.....
United Kingdom	23,538	.....	10,091
Tallow	212,680	852,849	.....
Whale fat, solid	14,386,000	13,823,400	440
SOAP AND CANDLES:			
Soap	40,785	336,368	1,170
Germany	.....	309,392	33
Russia	5,534	14,270	789
Sweden	19,484	10,988	326
Stearin candles	584	1,730	904
	Metric tons	Metric tons	Metric tons
ORES:			
Bismuth ore and other ores, n. e. s.	.....	10	.....
Chrome ore	20	2,737	2,395
Copper ore	74	2,175	809
Copper and nickel ore	.....	.....	.....
Iron ore and concentrates	373,071	187,805	150,960
Germany	189,596	152,454	135,814
Netherlands	90,345	.....	.....
United Kingdom	92,827	35,086	9,956
Briquettes	195,692	216,896	46,875
Germany	74,861	.....	.....
Sweden	2,512	.....	.....
United Kingdom	118,319	216,896	46,875
Lead ore	35	10	.....
Manganese ore	.....	22	.....
Molybdenum ore	5	141	201
Nickel ore	.....	.....	.....
Pyrite (iron and copper)	425,876	253,362	212,909
Belgium	26,251	.....	.....
Germany	40,892	84,511	4,105
Netherlands	46,773	10,145	8,914
Sweden	89,518	115,488	101,554
United Kingdom	138,134	21,844	50,770
Slag (rich in copper)	35,035	47,523	41,367
Belgium	399	.....	.....

[1] Not shown separately.

EXPORTS OF CHEMICALS AND ALLIED PRODUCTS (*Concluded*)

ARTICLES	1913 Pounds	1916 Pounds	1917 Pounds
ORES (*Concluded*):			
Pyrite slag (*Concluded*):			
Germany	2,974	4,031	3,925
Sweden	31,662	43,492	37,307
Rutile	51	82	114
Wolfram	.....	.....	2
Zinc ore	285	1	540
PAPER:			
Pounds	410,976,947	453,177,497	185,718,270
Value	$ 8,642,491	$15,601,272	$13,122,674
France	$7,826	$ 2,338,059	$615,944
Germany	$542,352	$25,380	$9,300
United Kingdom	$ 4,926,644	$ 6,090,809	$ 5,009,081
Australia	$618,356	$ 1,969,184	$ 1,945,439
British India	$191,406	$834,472	$ 1,303,257
China	$929,370	$762,808	$106,101
South America	$542,807	$ 1,699,120	$ 1,408,956
PULP AND CELLULOSE:	Metric tons	Metric tons	Metric tons
Cellulose, dry	209,544	216,800	133,564
Argentina	8,832	1,450	25
Belgium	12,064	.....	.....
France	22,803	32,839	6,905
Germany	7,613	.....	.....
Italy	3,666	8,111	3,206
Japan	5,124	8,923	.....
Mexico	3,344	51	.....
Netherlands	5,604	4,640	1,866
Spain	2,929	2,957	158
Sweden	2,952	3,966	1,260
United Kingdom	49,175	109,430	98,640
United States	77,777	40,331	19,855
Wet	1,634	5,540	3,169
Belgium	611	.....	.....
France	267	1,211	.....
United Kingdom	510	3,949	2,899
United States	.....	.....	30
Woodpulp, dry	14,661	12,962	17,319
Argentina	3,585	680	102
France	4,133	5,559	2,786
Spain	1,505	2,728	695
United Kingdom	1,608	1,303	11,195
United States	1,672	207	1,489
Wet	481,080	455,522	250,099
Belgium	46,992	.....	.....
Denmark	19,773	20,416	9,748
France	95,730	105,470	57,035
Netherlands	21,163	14,316	10,862
Spain	41	7,707	3,498
United Kingdom	295,210	302,418	148,861
United States	184	4,823	19,881
VARIOUS PRODUCTS:			
Glass	1,366,605	3,522,987	2,415,200
Glue	453,896	198,872	51,194
Pitch	549,718	606,644	251,569
Tar:			
Coal	6,392,898	1,394,732	1,064,877
Wood	106,854	119,975	21,605
Tar oil	9,057	20,948	.....
Vinegar and acetic acid	626	77	.....
Leather cream	1,433	109,188	9,085

ORIGINAL PAPERS

SOME CATALYSTS WHICH PROMOTE REACTION BETWEEN ANILINE AND ETHYL ALCOHOL[1]

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The facts and experimental data recorded in this publication have been obtained as the result of a preliminary research dealing with the interaction of ethyl alcohol and aniline hydrochloride. Our main object has been to obtain information leading to a better knowledge of the experimental conditions governing the formation of diethylaniline by direct alkylation with alcohol. The details of our investigation and the results obtained are discussed in the experimental part of the paper.

It has been known for several years that aromatic amines, of which aniline is the prototype, can undergo reactions with aliphatic alcohols if these reagents are heated together at high temperatures and under pressure. They interact to give products of two different types, namely, nitrogen substituted amines like monomethyl- and dimethylaniline, which are prepared commercially in large quantities, or true carbon derivatives resulting from substitution of the alkyl group in the aromatic nucleus of the amine. Para-ethylaniline is a representative of this second type of compound.[1] The molecular changes productive of these different compounds can be brought about by applying the alkylation reaction to a salt of the aromatic amine like aniline hydrochloride,[2] and also by heating the free amine with an alcohol in the presence of a strong dehydrating agent like zinc chloride,[3] or of certain catalysts which have been shown to promote such transformations.[1] The most important factors which regulate the course of the reaction with a given amine and alcohol are, apparently, the catalyst, and the temperature employed to bring about the change.

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[1] Researches on Amines, VII. The previous papers of this series have been published in the *Journal of the American Chemical Society*. Paper VI, *J Am. Chem. Soc.*, **38** (1916), 2507.

[1] Hoffmann, *Ber.*, **5** (1872), 720; **7** (1874), 527; **13**, 1729; **15** (1882), 1011, 1646, 2895; Pictet and Bunzl, *Ibid.*, **22** (1889), 1847; Studer, *Ann.*, **211** (1882), 237; Senkowski, *Ber.*, **24** (1891), 2975; Anschutz and Beckerboff, *Ibid.*, **28** (1895), 407; Willgerodt and Bergdolt, *Ann.*, **327** (1903), 286; Merz and Weith, *Ber.*, **14** (1881), 2346; Calm, *Ibid.*, **15** (1882), 1642; Louis, *Ibid.*, **16** (1883), 105, 116; **17** (1884), 1221; **21** (1888), 1159; Romburgh, *Rec. trav. chim.*, **3** (1884), 392; Sampaio, *Ber.*, **14** (1881), 2172; Benz. *Ibid.*, **15** (1882), 1646.

[2] Staedel, *Ber.*, **16** (1883), 30.

[3] Willgerodt and Bergdolt, *Loc. cit.*

While the operation of alkylating aniline directly with methyl alcohol to dimethylaniline has been developed to a high degree of efficiency, and is applied successfully on a very large scale commercially by heating the sulfate or hydrochloride of the amine with wood alcohol, the application of a similar reaction with amines and the higher aliphatic alcohols apparently has not been very successfully applied. In the case of aniline and ethyl alcohol, which is of particular interest to us at this time, Walther[2] writes as follows: "On the contrary, diethylaniline cannot be prepared with sulfuric acid." On the other hand, Staedel[3] claims to have obtained this tertiary amine in a nearly theoretical yield by heating the hydrobromide or hydriodide of aniline with ethyl alcohol at 150° C. Schultz and Julius[4] state that the same change can be brought about by using aniline hydrochloride for the reaction, but the product is less pure and contains a considerable amount of monoethylaniline.

There is apparently a definite temperature for each amine-alcohol mixture, above which it is impossible to obtain nitrogen alkylation if the reactions are applied in acid solution or in the presence of zinc chloride. This temperature reaches its maximum when alkylating with the lowest alcohol, namely, methyl alcohol. Application of the reaction at temperatures above this maximum leads to the formation of nucleus-substituted amines due to rearrangement, and it seems to be true that the tendency to rearrange from nitrogen to carbon is influenced by the size of the alkyl group of the alcohol. In other words, the larger the alkyl group of the alcohol the greater the tendency to rearrange in acid solution, and consequently the lower the temperature at which the formation of tertiary amines can be accomplished successfully.[5] These rearrangements have been the subject of much investigation, especially in the case of the action of methyl alcohol on aniline and its homologs.[6] The migrations in the majority of cases so far carefully examined are generally brought about by applying the reactions at temperatures above 250° C.

A careful review of the major researches on amine alkylation by heating with alcohols reveals the interesting fact that the investigator hitherto has generally proceeded to apply his reaction at a high temperature, namely, in the range of 250° to 300° C., or in some cases at much higher temperatures. The result has been that the product of his reaction has always been a nucleus-substituted compound, and in some cases the temperature has been sufficiently high to actually alter the constitution of the aliphatic group of the alcohol used. It seems also to have been quite general practice, when heating an amine directly with an alcohol, to introduce zinc chloride to accelerate the alkylation. This apparently promotes the splitting off of water and leads to the same results as are obtained by heating the salts of the amines with alcohol. In the case of reactions involving the use of methyl alcohol, which has received the most attention, the experimental data obtained indicate that temperatures below 230° C. are favorable for the formation of nitrogen derivatives. In the case of the higher alcohol homologs the optimum temperature for successful nitrogen alkylation in acid solution will undoubtedly be found to be lower than 230° C. The results obtained by Niementowski,[1] who investigated the behavior of aniline hydrochloride towards ethyl formate and ethyl acetate at 225° C., are in conformity with this statement.

If we confine our attention to the chemistry of aniline it appears, therefore, that any experimental conditions which favor the formation of alkyl halides as intermediate products of the reaction will lead to the production of nucleus-substituted amines if the alkylation reaction is applied at a higher temperature than 250° C. On the other hand, when experimental conditions are adopted which exclude the possibility of intermediate alkyl halide formation, it is possible to heat aniline with alcohols at much higher temperatures than 250° to 300° C. and obtain easily nitrogen derivatives without rearrangement of the alkyl group to the benzene nucleus. For example, Mailhe and de Gordon[2] have actually shown that mixtures of methyl alcohol and aniline vapors, when passed over thorium oxide, aluminum oxide or zirconium oxide at 400° to 500° C., interact smoothly to give mono- and dimethylaniline. They state that aluminum oxide is the best catalyst of the three oxides. In other words, under these conditions aniline interacts with alcohol in a manner similar to that of the corresponding reduced amine, hexaphenylamine, which was investigated by Sabatier and Mailhe.[3]

In this connection it is of special interest to call attention to the interesting observations made by by Knoevenagel[4] who has shown that the presence of traces of iodine promotes the reaction between aromatic amines and alcohols with formation of nitrogen alkyl derivatives. He obtained, for example, excellent yields of dimethyl- and diethylaniline by heating aniline with methyl and ethyl alcohol, respectively, in the presence of traces of iodine at 200° to 230° C. Not only did he apply his reaction successfully with aniline and amyl alcohol under these conditions, but he also showed that α- and β-naphthylamines behaved in a manner similar to aniline. In other words, no rearrangement of alkyl from nitrogen to carbon was observed in any case examined. These interesting observations of Mailhe and Knoevenagel suggest that quaternary nitrogen combinations functionate as intermediate products in the molecular rearrangements of secondary and tertiary aromatic amines into their isomeric carbon-substituted compounds.

In the light of these results of Knoevenagel it seemed probable to us that the reaction between aniline hydrochloride and ethyl alcohol might be stimulated by the introduction of certain reagents. So far as we are aware, no attention has been paid to the question of catalytic influences in such reactions. A research in this field seemed, therefore, very desirable both from a theoretical and a practical standpoint. The successful development of a method of operating which would be productive of diethylaniline in good yield, without recourse to ethyl bromide or ethyl chloride for alkylation, would be of the greatest practical interest. The results of our preliminary work on this problem are recorded in the following experimental part. The investigation is being continued and in our next paper we shall discuss experimental data obtained by working with the higher homologs of aniline.

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[1] Knoevenagel, *J. prakt. Chem.*, **89** (1914), 31.

[2] *Chem.-Ztg.*, **34**, 641.

[3] Staedel and Reinhardt, *Ber.*, **16** (1883), 30.

[4] "Organic Coloring Matters," p. 25.

[5] Niementowski, *Ber.*, **30** (1897), 3071.

[6] Hoffmann, *Loc. cit.*

[1] *Loc. cit.*

[2] *Compt. rend.*, **166** (1918), 467.

[3] *Ibid.*, **148** (1909), 898; **153** (1911), 621.

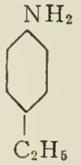
[4] *Loc. cit.*

EXPERIMENTAL

The experiments described in this paper were carried out in an iron autoclave of 1.7 liters capacity. This was constructed of heavy iron pipe and was furnished with a standard pressure gauge, thermometer well, and a glass or copper inset to avoid corrosion. The charge was heated by suspension of the autoclave in a bath of cottonseed oil. The procedure which was followed in all the experiments herein described was as follows: After the completion of the heating period the autoclave was allowed to cool and opened. The contents were transferred to a distilling flask and the excess of alcohol removed by heating at 100° C. under diminished pressure. A large part of the excess alcohol could thus be profitably recovered. The residual oil was then made strongly alkaline with sodium hydroxide in order to liberate the aromatic bases from their hydrochlorides, and steam-distilled. The amines were separated from the aqueous distillate by extraction with ether and the ether solution dried over fused sodium sulfate. After removal of the ether the oil was fractionally distilled at atmospheric pressure. The correct boiling point of monoethylaniline is 204° C. and that of diethylaniline is 215.5° C., at 760 mm.

During the preliminary experiments, and before the degree of alkylation of the aniline was observed to be notably raised by catalytic influence, a tolerably good idea of the success of any given experiment was gained by noting the range of distillation of the crude oil. We found, however, that a boiling point was no criterion of purity when oils containing 25 per cent and less of monoethylaniline were distilled. Constant boiling mixtures were always formed and it was absolutely necessary to analyze such oils.

The method which was used for the estimation of primary and secondary amines involved the use of acetic anhydride as a reagent. In brief this method is as follows: About one gram of the oil is weighed into a small flask having a ground glass neck. An equal, carefully weighed amount of acetic anhydride is added, and the flask, after being attached to a condenser provided with a ground glass connection, is heated for 30 min. on the water bath. Fifty cc. of distilled water are then carefully added through the condenser tube, and the mixture heated for 30 min. to hydrolyze the excess of acetic anhydride. After careful dilution in a graduated flask of convenient capacity an aliquot part is titrated with standard alkali solution in order to determine the excess of acetic anhydride. A blank experiment run under similar conditions standardizes the latter. The difference between the two analytical results is a measure of the acetylizable impurity in the oil. This is then calculated in terms of monoethylaniline. The aromatic bases which theoretically must be considered here together with diethylaniline are unaltered aniline, monoethylaniline, and nucleus-substituted amines such as ethylaniline and its monoethyl derivatives represented by Formulas I and II, respectively.



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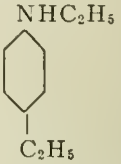

II

The proportion of these nucleus-substituted bases is increased by heating aniline with ethyl alcohol at high temperatures.

ACTION OF ETHYL ALCOHOL ON ANILINE IN THE PRESENCE OF CALCIUM OXIDE—Theoretically, the simplest procedure for the ethylation of aniline is that involving the interaction of this amine with alcohol. This reaction is typified by the equation

$$C_6H_5NH_2 + 2C_2H_5OH = C_6H_5N(C_2H_5)_2 + 2H_2O$$

and theoretically should be facilitated by the addition of a reagent capable of combining with water. So far as the writers are aware only one investigator has examined the influence of a basic oxide like calcium oxide on the activity of these two reagents. Calm[1] tried to bring about a reaction between amyl alcohol and aniline by heating these reagents in the presence of calcium oxide and also calcium chloride but reports that no change was effected by their presence. We have repeated this experiment with ethyl alcohol and our first set of preliminary experiments was therefore made with this oxide present as the dehydrating agent.

The autoclave charge was as follows:

Aniline	72 g.
Alcohol[2]	180 g.
Calcium oxide	100 g.
Time of heating	8 hrs.

Four runs were made at different temperatures and the results are recorded in Table I. Autoclave pressures were obtained as high as 500 and 700 lbs., but in no case was alkylation obtained under the conditions

TABLE I

No.	Aniline G.	Alcohol G.	Lime G.	Temperature ° C.	Time Hrs.	Product
1	72	180	100	150	8	Aniline
2	72	180	100	175	8	Aniline
3	72	180	100	200	8	Aniline
4	72	180	100	220–230	8	Aniline
5	72	180	No lime 10 g. KI and 2 g. iodine	150	8	Aniline

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[1] *Ber.*, **15** (1882), 1642.

[2] The alcohol used in all the experiments described in this paper contained about 1 per cent or less of water. It was prepared from ordinary 95 per cent alcohol by prolonged digestion with an excess of quicklime, until the desired gravity was attained.

described. In Expt. 5 potassium iodide and iodine were substituted as catalytic agents in place of calcium oxide and the mixture heated at a temperature of 150° C., but in this case also we obtained no evidence of the formation of alkylated derivatives.

ACTION OF ETHYL ALCOHOL ON ANILINE HYDROCHLORIDE—In the light of the results obtained by previous investigators, who have examined the behavior of ethyl alcohol toward aniline oil, we decided to confine our work to a study of the action of aniline hydrochloride on ethyl alcohol. Here we have a condition favorable for the production of ethyl chloride which is known to react with aniline with formation of alkyl derivatives. Aniline hydrobromide is far more reactive than the hydrochloride but is too expensive a reagent to use in manufacturing operations, while alkylation of aniline in the presence of sulfuric acid is not practical, due to the tendency of alcohol to undergo dehydration in the presence of this reagent giving ether and ethylene.[1]

While the question of alkylation of aniline by interaction of the halide salts of this amine with various alcohols has received much attention, no really satisfactory results have been obtained with ethyl alcohol, if one is to draw conclusion from what has been published in the chemical literature, as only generalized statements are available. The most productive results are those described in a publication by Staedel,[2] and which were obtained by application of a process patented by him.[3] He states that diethylaniline may be obtained in nearly quantitative yields by heating aniline hydrobromide or the corresponding iodide with a slight excess over two molecular proportions of ethyl alcohol at a temperature of 145° to 150° C. No description of a systematic series of alkylation experiments is recorded.

Concerning the use of aniline hydrochloride, only rather generalized statements are available in the literature in so far as they pertain to the synthesis of diethylaniline. For example, Schultz and Julius[4] state that diethylaniline is obtained by heating aniline hydrochloride and aniline with rather more than two moles of ethyl alcohol. The product contains a considerable quantity of monoethylaniline and in order to obtain the diethyl compound it is usually treated with sufficient ethyl bromide to complete the reaction. According to them this base is obtained more readily and in nearly theoretical yield by heating aniline hydrobromide with 2.2 moles of ethyl alcohol at 145° to 150° C.

In respect to the preparation of monoethylaniline these authors state that it is obtained by heating aniline hydrochloride or a mixture of aniline and hydrochloric acid with rather more than one mole of ethyl alcohol at 200° C. Cain[5] states the conditions for the preparation of mono- and diethylaniline as follows: For monoethylaniline, 95 parts of aniline hydrochloride and 28 parts of ethyl alcohol are heated together in an enameled autoclave at 180° C. for some hours. The product contains 70 to 73 per cent of monoethylaniline which crystallizes out as the hydrochloride. Diethylaniline may be prepared like monoethylaniline using aniline hydrochloride and ethyl alcohol. The product, however, contains a considerable amount of monoethylaniline.

In our experiments with aniline hydrochloride we first operated at the temperature recommended by Staedel in his work on the corresponding hydrobromide and hydriodide, namely, 150°. We applied the reaction under various conditions, using in some cases zinc chloride and calcium chloride as dehydrating agents, and also incorporating several reagents which we believed would exert a catalytic influence. It was found that the nature of the product was very much influenced by the presence of certain reagents. The results of our preliminary experiments are recorded in Table II.

TABLE II—INTERACTION OF ANILINE HYDROCHLORIDE AND ETHYL ALCOHOL

100 g. of aniline hydrochloride used in each experiment
Temperature, 150°
Time of heating, 8 hrs.
When $ZnCl_2$, $CaCl_2$, NaBr or KI were introduced as catalysts, 10 g. were always used

Expt.	$ZnCl_2$ or $CaCl_2$ 10 G.	NaBr or KI 10 G.	Moles of Alcohol	Special Catalyst	Total Yield	Distillate 195–200	200–204	204–206	206–208	208–210	210–214	214–216	216–218	218–220
1	...	...	2.2	....	87	..	24	24	27	9	..	..	..	..
2	...	...	5	....	87	40	26	8	6	..	..	..	..	..
3	...	NaBr	5	....	96	7	38	26	12	2	..	..	..	..
4	...	KI	5	....	96	6	37	26	14	2	..	..	..	..
5	$CaCl_2$	KI	5	....	..	..	..	72	5	..	..	..	..	..
6	$ZnCl_2$	KI	5	....	..	..	..	75	..	..	..	..	..	..
7	$ZnCl_2$	...	5	....	..	..	70	..	..	..	..	..	..	..
8	$ZnCl_2$	KI	10	....	..	..	..	..	73	..	14	..	..	..
9	$ZnCl_2$	KI	5	Copper lining	92	..	..	..	..	..	65	..	..	..
10	$ZnCl_2$	KI	5	Copper lining	93	..	..	..	..	..	70	..	..	..
11	$ZnCl_2$	KI	5	Copper strips	..	..	80	..	..	..	..	..	..	..
12	$ZnCl_2$	KI	5	5 g. CuO	..	..	63	..	..	..	17	..	..	..
13	$ZnCl_2$	KI	5	5 g. CuO + 8 g. HCl	..	..	65	..	19	..	..	..	..	..
14	$ZnCl_2$	KI	5	5 g. CuCl	..	42	3	..	..	..	..	..	..	..
15	$ZnCl_2$	KI	5	5 g. CuCl + 8 g. HCl	..	..	72	..	..	..	..	..	..	..
16	$ZnCl_2$	KI	5	3 g. $(C_6H_5)_2NH$	..	..	88	..	..	..	10	..	..	..
17	$ZnCl_2$	KI	5	5 g. $CuCl_2$	..	..	..	..	2	..	93	..	..	..
18	$ZnCl_2$	KI	5	5 g. $CuCl_2$	..	..	..	4	..	..	91	..	..	..
19	$ZnCl_2$	KI	5	5 g. $CuCl_2$ + 8 g. HCl	..	..	78	..	8	..	..	..	..	..
20	...	KI	5	5 g. $CuCl_2$	..	..	38	..	8	..	..	..	..	..
21	$ZnCl_2$	...	5	5 g. $CuCl_2$	..	..	..	..	16	..	46	..	..	..
22	...	...	5	5 g. $CuCl_2$	..	..	..	80	11	..	..	..	..	..

Expt. 1,[1] Table II, shows the result of substituting aniline hydrochloride for aniline hydrobromide under the conditions used by Staedel in the case of the latter salt. A theoretical yield of monoethylaniline would have been 92 g. Our product was very largely monoethylaniline. Nine grams of material boiling at 208° to 210° C. were obtained. Nothing, however, distilled within the range of diethylaniline. It is rather astonishing, in the light of Staedel's work, that diethylaniline was not more predominant in the reaction mixture. The use of 5 molecules of alcohol (Expt. 2) did not give as good a result. This is in some degree contradictory, for in the presence of a catalyst as well as at higher temperatures an increase of alcohol up to a certain limit is decidedly favorable in its effect.

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[1] Walther, *Chem.-Ztg.*, **34**, 641.

[2] *Loc. cit.*

[3] D. R. P. 21,241.

[4] *Loc. cit.*

[5] "The Manufacture of Intermediate Products for Dyes," p. 66.

[1] Except in special cases, the writers have considered it unnecessary to record in the tables the results obtained by duplication of their experiments. It should be understood that all experiments have been carefully checked, in particular where abnormalities occur. In Expts. 8, 19, and 20 the fractions indicated under column 206°–208° were collected from 206°–210°, and in Expt. 22 the fraction of 80 g. was collected between 202°–206°.

With the idea of obtaining a static condition similar to that existing when aniline hydrobromide or iodide is employed, 10 g. of sodium bromides (Expt. 3) and a similar amount of potassium iodide (Expt. 4) were introduced into the reaction mixture. An increased total yield was the result. The addition of 10 g. of calcium chloride as a dehydrating agent (Expt. 5) was likewise very favorable and slightly better than the former case, the total yield of monoethylaniline being of the order of 80 g. The substitution of zinc chloride (Expt. 6) for calcium chloride did not materially affect the result, whereas the omission of the iodide or bromide (Expt. 7) materially decreased alkylation. Increasing the alcohol factor to 10 moles (Expt. 8), together with the use of potassium iodide and zinc chloride, gave decidedly the best result yet obtained. For the first time a distillate boiling above 210° C. was obtained.

To summarize, the results of the first eight experiments recorded in Table II reveal the following facts:

1—That aniline hydrochloride when heated with 2.2 molecules of alcohol at 150° C. gives a product consisting largely of monoethylaniline, in contradistinction to Staedel's results, in which the use of aniline hydrobromide (or iodide) gave a product composed essentially of diethylaniline.

2—That the alkali bromides and iodides ($NaBr$ and KI) used in conjunction with the dehydrating effect produced by either calcium or zinc chloride, catalyze to a certain degree the ethylation of aniline.

3—That a large excess of alcohol is favorable for ethylation when used in the presence of the metallic salts.

During the course of our preliminary experiments it became necessary to employ a copper inset or lining in the autoclave, where a glass one had been used hitherto. The first two experiments (9 and 10) carried out with the copper lining gave rather good yields of diethylaniline. Since this lining had previously been used for other operations we had good reason to believe that the catalytic effects produced in our reaction might possibly be attributed to one of the following substances:

1—Metallic copper
2—Hydrochloric acid
3—Cuprous chloride
4—Diphenylamine
5—Cupric chloride

Experiments were therefore designed to establish the identity of the catalyst and were carried out in a glass inset; and a basic charge of 10 g. potassium iodide, 10 g. zinc chloride, 100 g. aniline hydrochloride, and 200 g. alcohol was used, together with the catalytic substance whose effect was sought.

The result recorded in Expt. 11 is typical of those obtained when strips of clean copper were placed in the charge, or when a thoroughly scoured copper inset was used. No catalytic effect similar to that observed in Expts. 9 and 10 was produced. Expt. 12 shows the effect of the addition of 5 g. of cupric oxide. The larger proportion of the reaction mixture was monoethylaniline. Expt. 13 was similar to 12 except in the fact that a little free acid was added (conc. HCl). The yield of monoethylaniline was increased, thus demonstrating the inhibitive effect of free hydrochloric acid on the final alkylation reaction.

A most striking inhibitive action was observed in Expt. 14 when cuprous chloride was employed. No diethylaniline was apparently formed and much unchanged aniline was present; this being evidenced by the fact that the bulk of the distillate boiled below 200° C. Somewhat more alkylation was observed in Expt. 15 when a small quantity of concentrated hydrochloric acid was added to the reaction mixture employed in Expt. 14. Expt. 16 shows the somewhat more favorable effect of diphenylamine as a catalyst. However, the yield of diethylaniline was insignificant.

Expt. 17 demonstrated very clearly the nature of the catalyst in that the addition of 5 g. of cupric chloride gave a most excellent yield of diethylaniline. This experiment was repeated (Expt. 18) and a similar result obtained. It is our conclusion, therefore, from these observations that the results obtained in Expts. 9 and 10 were due to the presence of cupric chloride in the slightly corroded containers used in these operations. The unfavorable effect of moisture, even when cupric chloride was employed, is shown in Expt. 19 where a small amount of concentrated hydrochloric acid was added to the charge.

An endeavor was made to obviate the use of either zinc chloride (Expt. 20) or potassium iodide (Expt. 21) when cupric chloride was used. Neither reagent could be omitted from the charge. However, the experiments did show the greater value of the zinc chloride as a catalyst as compared with the potassium iodide. The omission of both zinc chloride and potassium iodide (Expt. 22) gave no oil distilling within the range for diethylaniline.

The experimental work thus far reviewed established the fact that the autoclave charge when heated for 8 hrs. at a temperature of 150° C. would give a product consisting largely of diethylaniline. The autoclave pressures recorded in all these experiments carried out at 150° C. averaged about 190 lbs.

10 g. of zinc chloride
10 g. of potassium iodide
5 g. of cupric chloride
100 g. of aniline hydrochloride
200 g. of ethyl alcohol (99 per cent)

To summarize, the following substances were found either without appreciable effect, or slightly inhibitive in their action on the alkylation of aniline.

Without Effect	Inhibitive	Positive
Copper	Moisture-free HCl	Cupric chloride
Cupric oxide	Cuprous chloride	Diphenylamine

The next phase of our investigation which received attention was the proper temperature for efficient alkylation. Several experiments were run under the best conditions stated above and it was found that more consistent results, attended with better yields of diethylaniline, could be obtained by working at a constant temperature of 175° to 180° C. instead of 150° C. The results recorded in Expts. 1 and 2 of

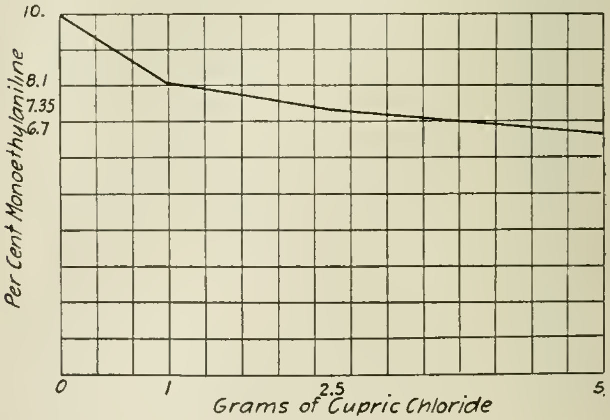

Fig. 1

TABLE III

									Distillate								
									M. E. A.					D. E. A.			
Expt.	$C_6H_5NH_2.HCl$. G.	$ZnCl_2$ or $CaCl_2$. G.	NaBr or KI. G.	Moles of Alcohol	Temperature. ° C.	Time	Special Catalyst G. $CuCl_2$	Total Yield	195–200	200–202	202–204	204–206	206–210	210–212	212–218	218–220	Monoethylaniline Per cent
1	100	10 $ZnCl_2$	10 KI	5	175–180	8	5	96	..	..	..	..	..	..	88	..	...
2	100	10 $ZnCl_2$	10 KI	5	175–180	8	5	96	..	..	..	..	..	..	88	..	...
3	100	10 $ZnCl_2$	10 NaBr	5	175–180	8	5	99	..	..	..	..	..	..	92	..	...
4	100	10 $CaCl_2$	10 NaBr	5	175–180	8	5	112	..	..	..	..	..	..	93	..	...
5	100	10 $CaCl_2$	10 NaBr	5	175–180	8	5	97	..	..	..	..	..	5	89	..	6.79
6	100	10 CaC_{12}	10 NaBr	5	175–180	8	None	83	..	..	..	..	2	..	72	..	10.00
7	100	10 $CaCl_2$	10 NaBr	5	175–180	8	2.59	105	..	..	..	..	3	..	95	..	7.35
8	100	10 $CaCl_2$	10 NaBr	5	175–180	8	1	96	..	..	..	..	3	..	88	..	8.10
9	100	10 $CaCl_2$	10 NaBr	8	175–180	8	5	103	..	..	..	..	..	..	90	..	6.70
10	100	10 $CaCl_2$	10 NaBr	10	175–180	8	5	100	..	..	..	..	1	..	94	..	5.00
11	100	10 $CaCl_2$	10 NaBr	14	175–180	8	5	90	..	..	..	..	..	..	83.5	..	7.60
12	100	10 $CaCl_2$	1 NaBr	10	175–180	8	5	85	..	..	..	..	3	..	77	..	11.08
13	100	10 $CaCl_2$	25 NaBr	10	175–180	8	5	90	..	..	..	..	3	..	84	..	11.6
14	100	10 $CaCl_2$	5 NaBr	10	175–180	8	5	92	..	..	..	..	2	..	87	..	7.7
15	100	10 $CaCl_2$	15 NaBr	10	175–180	8	5	100	..	..	..	..	..	..	84	..	7.1
16	100	20 $CaCl_2$	10 NaBr	10	175–180	8	5	105.5	..	..	..	..	..	..	92.5	..	10.5
17	100	5 $CaCl_2$	10 NaBr	10	175–180	8	5	100	..	..	..	..	..	..	87	..	9.4
18	100	10 $CaCl_2$	10 NaBr	10	175–180	4	5	95	..	..	..	..	..	22[1]	70	..	10.6
19	100	10 $CaCl_2$	10 NaBr	10	175–180	16	5	98	..	..	..	..	..	3	91.6	..	6.8
20	100	10 $CaCl_2$	10 NaBr	10	190	8	5	90.6	..	..	..	..	..	..	85	..	8.3
21	100	10 $CaCl_2$	10 NaBr	10	220	8	5	94	..	..	..	..	..	..	82	..	13.0
22	15 36	10 $CaCl_2$ Aniline	10 NaBr	10	175–180	8	5	..	..	..	69	..	..	..	11	..	M.E.A.
23	100	Aniline	10 NaBr	95% Alc.	175–180	8	5	96	..	..	24	..	..	..	91	..	12.24
24	100	20 $CaCl_2$	10 NaBr	95% Alc.	175–180	8	5	88	..	..	..	..	..	..	83	..	11.58

[1] The fraction was collected from 208–212.

Table III are representative of the effect of operating under such conditions.

Another phase of the investigation was concerned with the replacement of zinc chloride and potassium iodide by sodium bromide and calcium chloride (Table III). In Expt. 3, the substitution of sodium bromide for potassium iodide was productive of results wholly comparable with those obtained when potassium iodide was used, nor was the calcium chloride found to be less efficient than zinc chloride (Expt. 4). In other words, our results indicated that the conditions for reaction and the relative proportions of reagents best adapted for the preparation of diethylaniline were the following:

Calcium chloride	10 g.
Cupric chloride	5 g.
Sodium bromide	10 g.
Alcohol	200 g.
Aniline hydrochloride	100 g.
Temperature	175°–180° C.
Time	8 hrs.

Adopting a unit charge represented above as the basis for further work, a series of experiments were conducted in which the factors of concentration, time, and temperature were thoroughly investigated. The amount of cupric chloride productive of the best results was first ascertained, the other ingredients of the reaction mixture being kept constant in quantity. From inspection of Table III, as well as the curve developed from the same (Fig. 1), it may be seen that the effect of introducing cupric chloride is quite apparent even when small quantities are used (0–1 g.), the effect becoming gradually less pronounced up to 5 g., when a product containing but 6.79 per cent of monoethylaniline was obtained. This was the purest sample of diethylaniline that we had thus far obtained in our experiments. However, at this point it should be noted that the total yield as well as the 212° to 218° fraction was falling off in amount, due to the initiation of some decomposition from the presence of the excess of copper. This amount of copper chloride, however, was deemed the most efficient because it had promoted such a high degree of alkylation.

Four experiments were carried out, using alcohol as the variable factor. Five, eight, ten, and fourteen molecular proportions of alcohol were employed, corresponding to 160, 288, 360, and 504 g. of this reagent, respectively.

The curve for alcohol (Fig. 2) remains practically flat up to 8 moles; from here it falls sharply to 10 moles, where the monoethylaniline content of the oil was only 5 per cent, *the best product obtained in all our experiments.* Striking was the result, however, with the use of 14 moles, the purity of the product falling off to the extent of 7.9 per cent monoethylaniline. This is shown by the sharp rise in the curve from 10 to 14 moles.

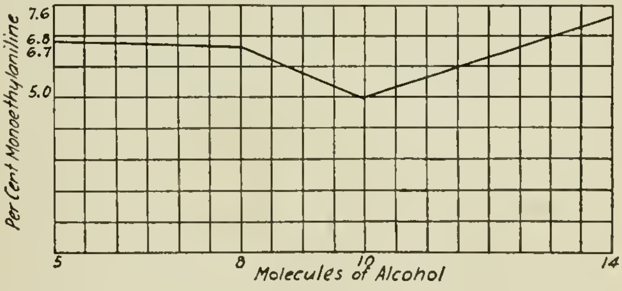

FIG. 2

With the following factors constant, sodium bromide was made the variable:

Aniline hydrochloride	100 g.
Alcohol	360 g.
Cupric chloride	5 g.
Sodium bromide (variable)	10 g.
Calcium chloride	10 g.
Temperature	175°–180°
Time	8 hrs.

Using but one gram of sodium bromide, the curve (Fig. 3) commences at a purity of 11 per cent monoethylaniline, rising slightly at 2.5 g. (presumably due to mechanical errors), then falls steadily with 5 and

10 g. of sodium bromide, reaching its lowest point with the latter figure. Further introduction of sodium bromide did not better the result, but if anything affected the purity, since the monoethylaniline content rose from 5 to 7.1 per cent. The effect of doubling the normal amount of calcium chloride is evidenced in the curve (Fig. 4) by an abrupt rise, denoting an increase in the acetylizable impurities, probably in the nature of *p*-ethyl substituted anilines. Using half the normal amount of calcium chloride was also unfavorable since incomplete alkylation was plainly manifest. In respect to concentration the following proportions of the catalysts were therefore the most efficient in their effect:

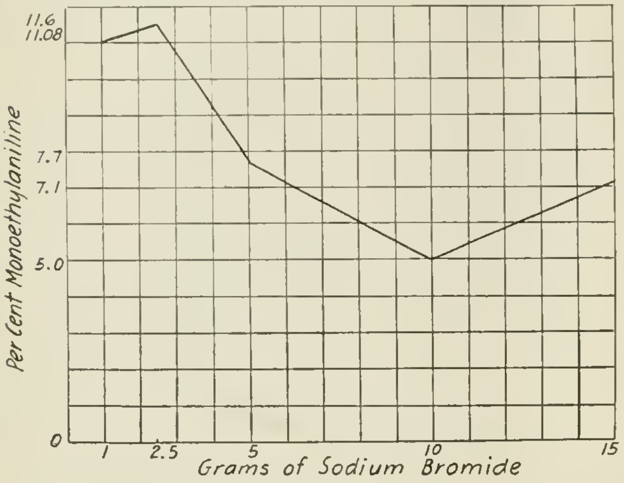

FIG. 3

	Grams
Sodium bromide	10
Cupric chloride	5
Calcium chloride	10

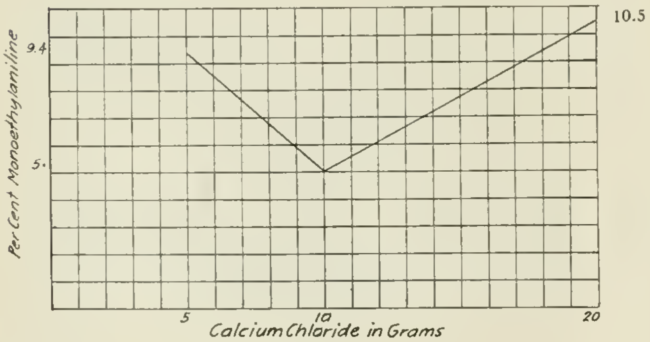

FIG. 4

The effect of time on the degree of alkylation is best shown in Fig. 5, where the highest point on the curve represents the percentage of monoethylaniline when heated for a period of 4 hrs. Incomplete reaction is evident in comparison with 8 hrs., the lowest point on the curve. Extension of the time factor beyond 8 hrs. was not productive of favorable results: in fact, at 16 hrs. the per cent of diethylaniline fell off slightly, showing the initiation of a reaction presumably typified by the expression

$$C_5H_5N(C_2H_5)_2 \longrightarrow C_2H_5.C_6H_4.NHC_2H_5.$$

In this case, in contradistinction to the 4-hr. period, the acetylizable material very probably is a nucleus-substituted derivative of aniline and not unchanged aniline.

It was our experience that temperatures below 175° C. made for results not as consistent as those obtained when the higher temperature was employed. The question as to whether the optimum temperature was above 175° C. was next investigated. The temperature of 190° C. (see Fig. 6) caused a rise in the acetylizable impurities. This fact could be attributed only to rearrangement of the tertiary amine through the influence of the metallic salts at the elevated temperature. This effect was even more striking at 220° C., when the impurity calculated as monoethylaniline rose to 13 per cent.

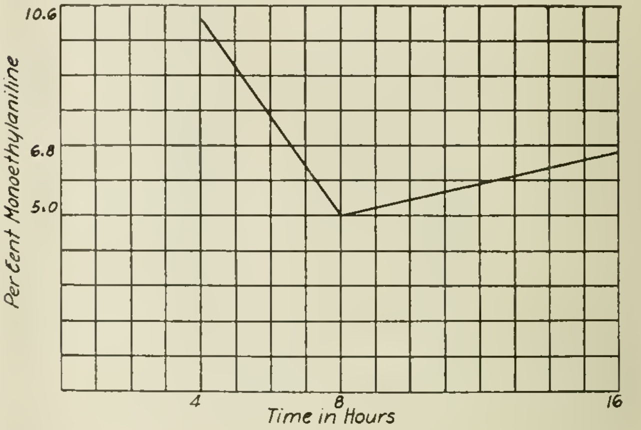

FIG. 5

To summarize, the results obtained in our experimental work have led us to conclude that sodium bromide, cupric chloride and calcium chloride jointly functionate as catalytic agents in the alkylation of aniline when the hydrochloride of this base is heated with ethyl alcohol. The relative proportions of the various reagents and the time and temperature factors which are productive of the maximum yield of the tertiary base—diethylaniline—are given in the following table representing a unit autoclave charge. A unit charge run at a temperature of 175° to 180° is productive of pressures in the autoclave varying between 280 and 310 lbs.

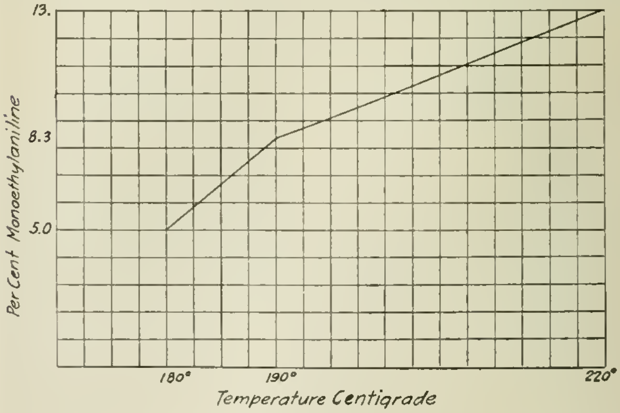

FIG. 6

Aniline hydrochloride	100 g.
Alcohol	10 moles (360 g.)
Sodium bromide	10 g.
Cupric chloride	5 g.
Calcium chloride	10 g.
Time	8 hrs.
Temperature	175°–180° C.

We have run through a great many experiments under the above conditions and they have all been productive of good yields of diethylaniline. The yields have always been very consistent. The total yield is more frequently above (*i. e.*, 104–105 g.) than below 100 g. Complete alkylation, together with complete extraction of the alkylated material, should produce the theoretical yield of 115 g. Therefore, notwithstanding the many opportunities for mechanical losses, decomposition through autoclave heat, to say nothing of the purity of the commercial aniline hydrochloride, crude yields of the order of 87 to 91 per cent are consistently obtainable.

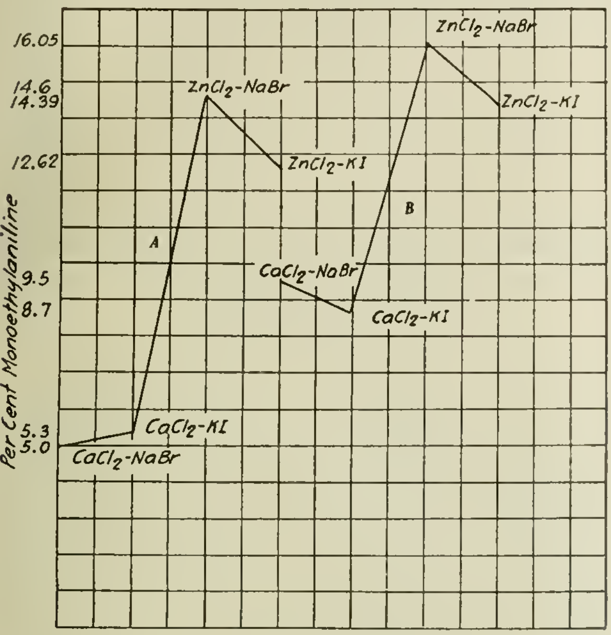

FIG. 7

Generally speaking, in the distillation of the crudes resulting from these best operative conditions, no oil, other than a drop or two, is obtained below 212° C. The loss of material in distillation is largely accounted for in the residue left in the flask, no doubt resulting from some decomposition during the distillation. The product, purified by distillation, is always a clear, highly refractive oil, possessing a slight yellow color.

An attempt was made to lower the cost factor in the production of diethylaniline by our method, through the incorporation of some aniline base in place of the hydrochloride, and also through the use of 95 per cent alcohol. The substitution of aniline oil for an equivalent amount of the hydrochloride in our best unit charge gave a product consisting largely of monoethylaniline (Expt. 22). The use of 95 per cent alcohol (Expt. 23) instead of the product dehydrated over lime lowered the purity about 7 per cent; nor could this be prevented by the incorporation of double the usual amount of calcium chloride as a dehydrating agent (Expt. 24).

As previously stated, calcium chloride and sodium bromide had been utilized in place of zinc chloride and potassium iodide, respectively, purely from the standpoint of economical procedure. In the light of this fact it seemed of interest to ascertain the relative efficiency of these salts. The efficiency of zinc chloride as compared with calcium chloride is shown in Fig. 7 (also Table IV), where Graph A represents the effects produced when the usual amounts of the catalysts are used. The second Graph (B) represents the effect when the amount of calcium chloride is reduced one-half, and also the sodium bromide or potassium iodide. The nature of the two results should check. At the peak of each curve stands zinc chloride and sodium bromide with zinc chloride and potassium iodide just below it, while at the inception of Curve A stands calcium chloride and sodium bromide, with calcium chloride and potassium iodide slightly above it. In Graph B the conditions are reversed. The results may therefore be summed up in the statements, first, that zinc chloride is much less efficient than calcium chloride in alkylation, and, second, that the iodide is but slightly different in its effectiveness as compared with the bromide. Placing more emphasis on the zinc chloride results, the conclusion may be reached that the potassium iodide functions somewhat more favorably than the sodium bromide.

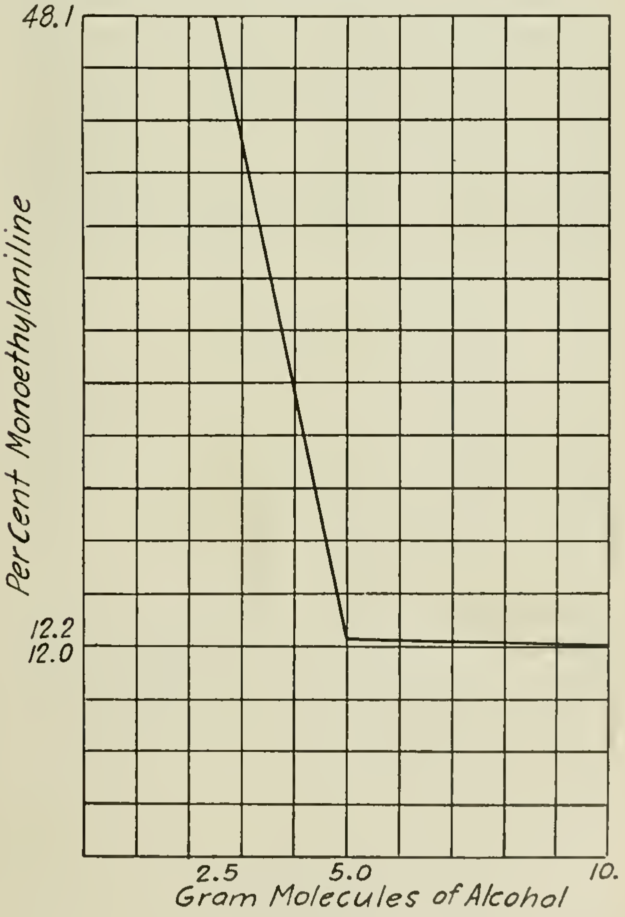

FIG. 8

In regard to the zinc chloride, it may be said in explanation of its action, that in all probability it

TABLE IV

100 g. of aniline hydrochloride were used in each experiment. The quantity of $ZnCl_2$ and $CaCl_2$ introduced was always 10 g., and the time of heating the autoclave was 8 hrs. In each experiment the temperature was held between 175°–180° C.

						Distillate											
						M. E. A.						D. E. A.					
Expt.	$ZnCl_2$ or $CaCl_2$	Grams NaBr or KI	Moles of Alcohol	Grams Special Catalyst	Total Yield. G.	195–200	200–202	202–204	204–206	206–208	208–210	210–212	212–214	214–216	216–218	218–220	Monoethylaniline Per cent
1	$ZnCl_2$	10 NaBr	10	5 $CuCl_2$	101.3	..	..	..	..	..	2.5	..	..	95.8	..	..	14.6
2	$ZnCl_2$	10 KI	10	5 $CuCl_2$	90	..	..	..	..	..	1·3	..	..	85	..	..	12.62
3	$ZnCl_2$	10 KI	10	5 $CuCl_2$	100.4	..	..	..	..	..	0.8	..	..	95	..	..	5.3
4	$ZnCl_2$	5 NaBr	10	2.5 $CuCl_2$	94	..	..	..	..	..	1.6	..	..	89.3	..	..	9.5
5	$ZnCl_2$	5 KI	10	2.5 $CuCl_2$	96	..	..	..	..	..	0.3	..	..	91.8	..	..	8.7
6	$ZnCl_2$	5 NaBr	10	2.5 $CuCl_2$	96.3	..	..	..	..	..	6.8	..	..	86	..	..	16.05
7	$ZnCl_2$	5 KI	10	2.5 $CuCl_2$	80	..	..	..	..	..	..	..	..	75	..	..	14.39
8	....	....	2.2	....	80	..	..	..	..	12	26	16	9	3	3	..	48.1
9	....	....	5	....	93	..	..	..	..	..	..	7	57	4	2	..	12.2
10	....	....	10	....	103	..	..	..	..	..	1	6	55	29	6	..	12.0
11	....	10 NaBr	10	....	102	..	..	..	..	..	..	..	55	39	4	..	10.2
12	....	....	10	5 Pyridine	99	..	..	..	..	1	0.5	8	44	35	9	..	15.9
13	....	....	10	5 Cu Powder	93	..	..	..	..	..	..	1	24	48	11	..	8.6

functions at a high temperature as a de-alkylating, as well as a dehydrating agent, and the smaller yield of diethylaniline produced by it in comparison with calcium chloride may be due to the fact that this salt rearranges some of the diethylaniline formed to a nucleus-substituted amine, such as the monoethylated derivative of *p*-ethylaniline or similar combinations.

Expts. 1 and 2 of Table II are illustrative of the results obtained by heating aniline hydrochloride alone with alcohol at 150° C. In these experiments the concentration of the alcohol was 2.2 and 5 moles, respectively. In neither case was there any distillate within the range for diethylaniline. Expts. 8, 9, and 10 of Table IV furnish very interesting comparisons, when the reaction temperature of 175° to 180° C. is employed. Expt. 8 gave a product containing but 51.9 per cent diethylaniline, yet even this result was distinctly better than the corresponding experiment carried on at 150°, while an increase of alcohol to 5 (Expt. 9) and 10 moles (Expt. 10) decreased the monoethylaniline content to a marked degree. These results, shown graphically in Fig. 8, are very noteworthy, in that they demonstrate again the extremely favorable effect of the concentration of alcohol on the ethylation of aniline.

The introduction of 10 g. of sodium bromide to the most favorable alcohol concentration lowered the monoethylaniline content some 2 per cent, while the addition of 5 g. of pyridine (Expt. 12) produced a rather marked negative catalysis in that 15.9 per cent of the product was monoethylaniline.

Although we have been unable to better the results obtained (5 per cent monoethylaniline impurity) when the three inorganic salts are used, mention should be made of one very interesting experiment (Expt. 13) in which the addition of 5 g. of copper powder and sodium bromide to the usual amounts of aniline hydrochloride and alcohol gave a product containing but 8.6 per cent monoethylaniline. This result is rather interesting in the light of the experiment mentioned in the first part of the paper, when clean copper strips or a thoroughly cleaned copper inset were apparently without catalytic effect. The difference in results may of course be attributed to the state of division of the copper.

THE EFFECT OF AIR IN STEAM ON THE COEFFICIENT OF HEAT TRANSMISSION

By C. S. Robinson

MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASS.

Received March 9, 1920

Recently the writer had occasion to discuss the effect of the presence of non-condensable gases in condensable vapor on the coefficient of heat transmission. A study of the data in the literature[1] showed that the information was not in a readily usable form, and that it was necessary to refigure it. The writer feels that the results of these recalculations will be of interest to engineers and that a presentation of the methods of calculation used may be of assistance to others who have similar problems to be solved. It should be emphasized that the relations hereinafter derived are approximate, and are based on very incomplete data. Until more information is available, they are, however, the best to be had.

The flow of heat from one point to another is inversely proportional to the thermal resistance of the material between the two points. Where the material in the path of flow is not homogeneous, but is made up of successive sections having different resistances, the method used in calculating the over-all resistance is the same as that used in electricity, that is, the over-all resistance is the sum of the resistances of the successive sections.

In the special cases of the surface condenser and the evaporator, the heat flows from the condensing vapor to the separating wall, through this wall, and from the further side of the wall to the cooling fluid, which in the first case is the condenser water, and in the second, the boiling liquid. The coefficient of heat transfer from the vapor to the cooling fluid may be calculated, providing the resistances of the successive sections of the path are known. These sections are: first, the film resistance on the vapor side; second, the resistance of the metal; and third, the film resistance on the liquid side.

The conductivity of metals has been carefully studied, and it is possible to obtain values of the coefficient of the metal from such handbooks as Kent and Marks. The film resistance on the liquid side has also been the subject of careful experimental work. It has been found that this resistance is largely a function of the liquid velocity, and recent work done at the Massachusetts Institute of Technology (not yet published) would indicate that the coefficient of conductivity of the film on the liquid side, h_e (the reciprocal of the resistance), may be calculated closely from the equation

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[1] E. W. Kerr, "Tests upon the Transmission of Heat in Vacuum Evaporators," *Trans. A. S. M. E.*, **35** (1913), 731; G A. Orrok, "Air in Surface Condensation," *Ibid.*, **34** (1912), 713; J. A. Smith, "Effect of Air in Feed Water," *London Engineering*, Oct. 7, 1904.

$$h_e = 450\text{V}^{0.8},$$

where h_e is in B. t. u. per sq. ft. of heating surface per deg. F. temperature difference per hr., and $\bar{\text{V}}$ is the linear velocity of the liquid through small pipes (up to 2 in. diameter) in ft. per sec.

The film coefficient on the vapor side, however, has had less careful study. It has long been known that it has been largely affected by such factors as

1—Steam velocity past the heating surface
2—Steam pressure
3—Rate of condensation
4—Rate of removal of condensed steam
5—Presence of non-condensable gases

The last of these factors is of very great importance and is the one in which the writer was particularly interested.

Of the information available from the three articles mentioned above, that in Professor Kerr's article proved to be the only one with the data in such condition that it could be analyzed with respect to the film conductivity on the steam side, and the following calculations are based almost entirely on his data. His experiments were made with an experimental, vertical, tubular evaporator, with water inside the tubes. The pressure and temperature of the vapor in the steam belt were measured, and from the latter the partial pressure of the water vapor in the mixture of steam and air was determined with the aid of steam tables. The ratio of the partial pressure of the water vapor to the total pressure was calculated and tabulated against the coefficient of heat transmission of the evaporator. This ratio multiplied by 100 is equal to the percentage by volume of the water vapor in the mixture, and in Table 1 it is so recorded.

TABLE I

Steam by Volume Per cent	Coeff. of Heat Transmission	Film Coeff. Steam Side	y	Film Coeff. Water Side
100	594	3000 (assumed)	4.55	757
100	533	3000 (assumed)	4.35	658
99.7	510	2500 (calculated)	4.45	650
97.3	464	2080 (calculated)	4.45	606
93.1	487	2270 (calculated)	4.45	628
91.6	408	1720 (calculated)	4.45	541
91.3	386	1510 (calculated)	4.45	523
90.9	300	1030 (calculated)	4.45	427
82.2	296	1010 (calculated)	4.45	421
81.1	284	970 (calculated)	4.45	405
74.2	258	830 (calculated)	4.45	377
74.4	241	740 (calculated)	4.45	360
72.4	215	640 (calculated)	4.45	324
72.1	240	750 (calculated)	4.45	356
67.6	179	500 (calculated)	4.45	281
66.8	147	377 (calculated)	4.45	242

The film coefficient of heat conductivity on the steam side is calculated from the expression

$$\frac{1}{\text{K}} = \frac{1}{h_s} + \frac{1}{k_m} + \frac{1}{h_e},$$

where K is the over-all coefficient of the evaporator, h_s is the film coefficient on the steam side, k_m is the coefficient of the given metal wall, h_e is the film coefficient on the liquid side.

In the data referred to, K only is known. It is, however, possible to approximate values for k_m and h_e. The metal wall used was copper 0.05 in. thick. The heat transmission of copper is 220 B. t. u. figured as per foot of thickness. Therefore,

$$k = \frac{220 \times 12}{0.05} = 53{,}000\text{—a relatively large quantity.}$$

The film coefficient for steam containing no gases is stated by various writers to lie between 2000 and 4000. It is known that vertical tubular evaporators, when boiling water under test conditions, have given over-all coefficients of 1500. This would indicate that the film coefficient on the steam side was not less than double 1500, or 3000. The writer has taken this last value as the mean of the limits noted above, and as very probably near the true one for the conditions of the experiment.

The first test would then give the expression

$$\frac{1}{594} = \frac{1}{3000} + \frac{1}{53000} + \frac{1}{h_e}.$$

The phenomena occurring in a vertical evaporator tube are well understood. The liquid at the lower end contains no vapor, and has relatively low velocity. The evaporation and therefore the volume of vapor increases as the liquid rises, and the mixture of vapor and liquid issuing from the top does so under maximum velocity. The film conductivity on the liquid side is some function of this velocity as noted above. Since $h_e = f(\bar{\text{V}})$ and $\text{K} = f'(\bar{\text{V}})$, then it may be stated approximately that $h_e = f''(\text{K})$ since the greater the flow of heat, the greater the amount of vapor formed, and the greater the vapor velocity, and the writer has selected this function as $h_e = y\text{K}^{0.8}$.

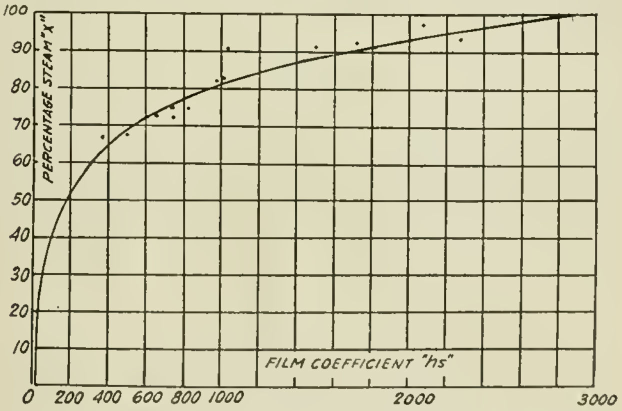

FIG. I—SHOWING RELATION BETWEEN FILM COEFFICIENT FOR CONDENSING VAPOR AND PERCENTAGE STEAM IN STEAM-AIR MIXTURES

$$\frac{1}{594} = \frac{1}{3000} + \frac{1}{53000} + \frac{1}{y(594)^{0.8}}$$

$$\therefore y = 4.55$$

Repeating this calculation for the second test

$$y = 4.35.$$

The writer selected the mean, 4.45, as the value of y to use in the balance of the tests when air was present in the steam. Test 3 would then give the following:

$$\frac{1}{510} = \frac{1}{h_s} + \frac{1}{53000} + \frac{1}{4.45(510)^{0.8}}$$

$$h_s = 2500$$

Table I gives the results of the calculation for all of the tests. Fig. I shows values of percentage of steam plotted against film coefficient—h_s.

The data include steam percentages down to 66 per cent only. The film coefficient for zero per cent, that is, all air, has been the subject of much careful work, the values of h being a function of the velocity and varying between 1 and 20. Since no information was given in Professor Kerr's experiments as to the rate of removal of the air, the writer selected a mean value of 10 for this point in order that it might be possible to derive a suitable empirical equation to fit the above calculation.

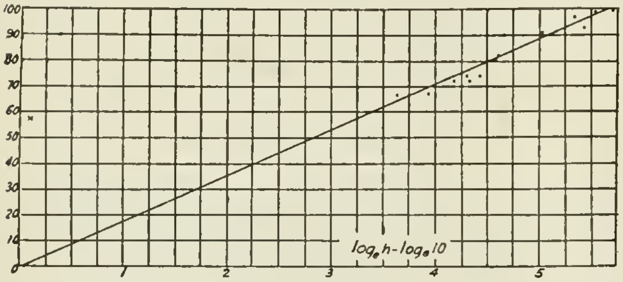

FIG. II—EFFECT OF AIR ON "L" FOR STEAM: x = PER CENT STEAM BY VOLUME, h = FILM COEFFICIENT

Inspection of the curve on Fig. I indicates that it has the form indicated by the exponential equation

$$h = ae^{\beta x},$$

where a and β are constants to be determined and x is per cent steam by volume. In order to test the applicability of this type of equation, it may be rectified as follows. Take the logarithm of both sides of the equation

$$\log_e h = \log_e a + \beta x.$$

If a plot of the data in the form of ($\log_e h - \log_e a$) versus "x" indicates a straight line, the equation selected is satisfactory. Since when $x = o$, $h = a$, $\therefore a = 10$, and the resulting plot is shown on Fig. II.

The proper value for β was found by averaging all of the points, the resulting equation having the form

$$\log_e h = 2.303 + 0.0566x$$

or

$$h = 2.303\, e^{0.0566x}$$

a more convenient form of the equation is

$$\log_{10} h = 1 + 6.0240x.$$

A plot of this equation is represented by the curve on Fig. I.

THE PRODUCTION OF PHOSPHORIC ACID BY SMELTING PHOSPHATE ROCK IN A FUEL-FED FURNACE

By William H. Waggaman and Thomas B. Turley

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[PRELIMINARY REPORT]

Received March 1, 1920

Ever since the early days of the war when the high cost and scarcity of acid phosphate seemed to menace our agricultural interests, the Bureau of Soils has given considerable attention to the production of soluble phosphates by means other than the usual method of treating phosphate rock with sulfuric acid.

Perhaps the most attractive and in many ways the most promising of these processes is that in which an intimate mixture of a natural phosphate, silica, and coke is smeltered at a high temperature, with the result that silicates of lime are formed and the phosphoric acid volatilized and subsequently collected in some suitable manner. This process is really based on the method long in use for the manufacture of phosphorus, and in order to separate completely the phosphoric acid from the lime it is apparently necessary to have a sufficient quantity of reducing agent present to produce elementary phosphorus according to the equation

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C = 3CaSiO_3 + 2P + 5CO.$$

The phosphorus produced is subsequently burned or oxidized within or outside of the furnace by carbon dioxide or air thus

$$2P_2 + 5O_2 = 2P_2O_5$$

or

$$P_2 + 5CO_2 = P_2O_5 + 5CO.$$

It has been generally believed that the temperature and other conditions necessary to volatilize completely phosphorus and phosphoric acid from natural phosphates could be attained only in the electric furnace,[1] and the Bureau's early experiments were therefore conducted in furnaces of the arc type. As the results of these investigations have been described in previous articles, only a brief outline of the work is given in the present paper.

The first experiments were carried on in a rather crude electric furnace constructed at the Bureau's experimental laboratories at Arlington Farm, Va., and here the Cottrell method of electrical precipitation was first successfully applied to the collection of the volatilized phosphoric acid. Ross, Carothers and Merz[2] showed that by this means there could be obtained an acid of such high concentration that the added cost of manufacturing phosphoric acid by the volatilization process would be partly offset by the saving in transportation charges in shipping and distributing the product. Later a larger and more complete furnace with auxiliary apparatus was constructed at Hoboken, N. J.

In reporting on this work Carothers[3] showed that, assuming the price of electric power at $25 per h.-p. yr., phosphoric acid (P_2O_5) could be produced and recovered at a cost of 3.37 cents per pound exclusive of interest on investment, taxes, and royalties. By using the acid thus obtained to treat more phosphate rock, however, a double superphosphate could be produced which brought down the price of the unit of soluble phosphoric acid very appreciably. The figures indicated that under the abnormal conditions existing at that time, the cost per unit of phosphoric acid produced by the volatilization process compared favorably with the cost of this ingredient in ordinary superphosphate obtained by the sulfuric acid method.

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[1] F. S. Washburn, U. S. Patents 1,044,957 (1912); 1,100,639 (1914).

[2] THIS JOURNAL, **9** (1917), 26.

[3] *Ibid.*, **10** (1918), 35.

TABLE I—VOLATILIZATION OF PHOSPHORIC ACID FROM MIXTURES OF TRICALCIUM PHOSPHATE, SILICA, COKE AND ALUMINA BY SMELTING IN OPEN AND CLOSED CRUCIBLES IN A DENTAL FURNACE BY MEANS OF ILLUMINATING GAS AND AN AIR BLAST

Sample No.	Crucible	Proportions of Materials Used in Charge				Percentage Composition					Temperature Attained ° C.	Length of Time Heated Hrs.	P_2O_5 in Slag Per cent	P_2O_5 Volatilized Per cent of Total	Character of Slag
		$Ca_3(PO_4)_2$ Grams	SiO_2 Grams	Al_2O_3 Grams	Coke Grams	SiO_2	CaO	Al_2O_3	P_2O_5	C					
12 A.....	Closed (Clay)	20.0	16.6	...	5.2	40.7	25.9	0.7	21.9	10.8	Above 1400	0.75	3.24	89.8	Fluid, grayish black
12 G....	Open (Clay)	20.0	16.6	...	5.2	40.7	25.9	0.7	21.9	10.8	Above 1400	1	7.20	76.2	Viscous gray. White bloom on surface[1]
12 N_1....	Open (Graphite)	20.0	16.6	6.6	5.2	35.1	22.4	14.3	18.9	9.3	1200	1	4.92	80.4	Viscous black
12 N_2....	Open (Graphite)	20.0	16.6	6.6	5.2	35.1	22.4	14.3	18.9	9.3	Above 1400	2	None	100.0	Fluid, black
12 O.....	Open (Clay)	20.0	16.6	...	4.8	41.1	26.2	0.7	22.1	9.9	Above 1400	1	3.36	89.3	Fluid, light gray
12 P.....	Open (Clay)	20.0	16.6	6.6	5.0	40.9	26.1	0.7	22.0	10.3	Above 1400	1	2.22	93.0	Fluid, light gray; bloom on surface[1]
12 Q.....	Open (Clay)	20.0	16.6	6.6	5.4	40.7	25.8	0.7	21.8	11.0	Above 1400	0.75	4.65	84.9	Fluid, light gray; bloom on surface[1]
12 R....	Open (Clay)	20.0	16.6	6.6	5.6	40.5	25.7	0.7	21.7	11.4	Above 1400	0.75	2.45	92.2	Fluid, light gray; bloom on surface[1]
12_1......	Open (Clay)	20.0	16.6	6.6	5.2	40.7	25.9	0.7	21.9	10.4	1300	1	Trace	100.0	Fluid, light gray; large bloom[1]
12_2......	Closed (Clay)	20.0	16.6	6.6	5.2	40.7	25.9	0.7	21.9	10.4	1300	1	Trace	100.0	Fluid, all slag
12_{11}......	Open (Clay)	20.0	16.6	2.0	5.6	38.7	24.5	5.2	20.7	10.9	1300	1	5.28	81.3	Viscous light gray; bloom on surface[1]
12_{12}......	Closed (Clay)	20.0	16.6	2.0	5.6	38.7	24.5	5.2	20.7	10.9	1300	1	1.91	93.6	Viscous dark; no bloom
12_{15}......	Open (Clay)	20.0	20.0	2.0	4.8	43.6	23.2	4.9	19.6	8.7	1300	1	4.26	83.7	Viscous gray; large bloom[1]
12_{16}......	Closed (Clay)	20.0	20.0	2.0	4.8	43.6	23.2	4.9	19.6	8.7	1300	1	3.52	86.6	Viscous gray; no bloom
12_{17}.....	Open (Clay)	20.0	22.0	2.0	4.8	45.9	22.2	4.7	18.8	8.4	1300	1	3.90	84.3	Viscous gray; large bloom[1]
12_{16}.....	Closed (Clay)	20.0	22.0	2.0	4.8	45.9	22.2	4.7	18.8	8.4	1300	1	3.75	84.8	Viscous gray; no bloom

[1] An analysis of the bloom or white crust on the surface of slags obtained in open crucibles shows a considerably higher percentage of phosphoric acid than in the original mixture. The proportion of lime to phosphoric acid coincided very closely with that in calcium pyrophosphate ($Ca_2P_2O_7$).

In a later investigation, Waggaman and Wagner[1] pointed out that by using the "mine-run" phosphates of Florida, which in their natural state contain impurities which preclude their treatment with sulfuric acid until they have been put through an elaborate washing and screening process, a great saving in phosphate could be effected and the cost of the soluble phosphoric acid produced therefrom very materially reduced.

The high cost of electric power in this country, however, made it appear very desirable to test out the commercial possibilities of producing phosphoric acid for fertilizer purposes in a fuel-fed furnace, and, since crude oil is the cheapest and most accessible fuel for the phosphate regions of Florida, it was decided to undertake experiments with a view to producing phosphoric acid by this means.

LABORATORY EXPERIMENTS

Preliminary work in the laboratory, where various mixtures were heated in a dental furnace by means of gas and an air blast, showed that contrary to general opinion the nearly complete evolution of phosphoric acid from a charge of calcium phosphate, carbon and quartz flour was perfectly feasible provided that reducing conditions were maintained until a fusible slag was produced, and a temperature of approximately 1500° C. was continued throughout the operation.

Table I shows in part the results obtained by heating such mixtures, with and without the addition of small amounts of aluminum oxide, in both open and closed fire-clay crucibles.

An inspection of Table I will show that as a rule considerably better results were obtained where the crucibles were kept covered so that the oxidizing gases were not allowed to come into contact with the charge. When the crucibles were left open, it was noticed that a white crust or "bloom" almost invariably formed over the slag and no matter how long the high temperature was maintained this crust gave no sign of melting. The quantity of this crust in a number of instances was equal to that of the underlying slag. It is assumed that the phosphoric acid distilling from the lower part of the mass recombined with or was fixed by the lime at the surface where oxidizing conditions prevailed, forming calcium pyrophosphate according to the following equation:

$$2Ca_3(PO_4)_2 + P_2O_5 = 3Ca_2P_2O_7$$

It was found, however, that when the fusion of the charge was well under way and the carbon or coke thus protected in the mass of molten slag, the covers of the crucibles could be removed without the formation of this crust and that the reaction continued in spite of the oxidizing conditions at the surface of the slag. The addition of small amounts of alumina to the charge seemed to aid the fusion somewhat, it being a well-known fact that the presence of this substance in limited amounts lowers the melting point of both acid and basic slags.

In most of these mixtures the ratio of silica to lime was approximately 39 to 61 per cent, but it was found later, in dealing with the natural phosphates of Florida, that better results could be obtained by varying these proportions according to the composition of the mineral used.

These laboratory experiments pointed almost conclusively to the necessity of maintaining reducing conditions in the phosphatic charge until fusion has begun, and it appeared at first sight that the most practical method of doing so in a mass containing much finely divided material, such as the pebble phosphates and the mine-run phosphates of Florida, was to heat the mixture in a separate chamber so that the oxidizing gases from the burning fuel would not come into contact with the charge until the latter had been brought to a state of incipient fusion.

LARGER SCALE EXPERIMENTS

Accordingly in order to test this process on a semi-commercial scale, a fire-brick furnace of the type shown in Fig. 1, described by the senior author and others in U. S. Patent 1,282,994, was constructed at Arlington Farm, Va. This furnace comprised a central or inner chamber (holding about 150 lbs. of charge) open both at the top and bottom but constricted somewhat at its lower end to prevent the charge from working through too rapidly. This chamber was supported on arches of carborundum brick above a hollow hearth intended to receive the molten silicate. The whole was surrounded by an outer chamber into the opposite walls of which were set two oil burners so placed that their flames played upon and around the lower part of the inner chamber, heating the charge by radiation through the 4-in. walls. Any fumes which were evolved from the smelting of the mass were to be drawn down through the charge chamber and passed together with the gases of combustion onto the Cottrell precipitator in order to collect the phosphoric acid.

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[1] THIS JOURNAL, 10 (1918), 353.

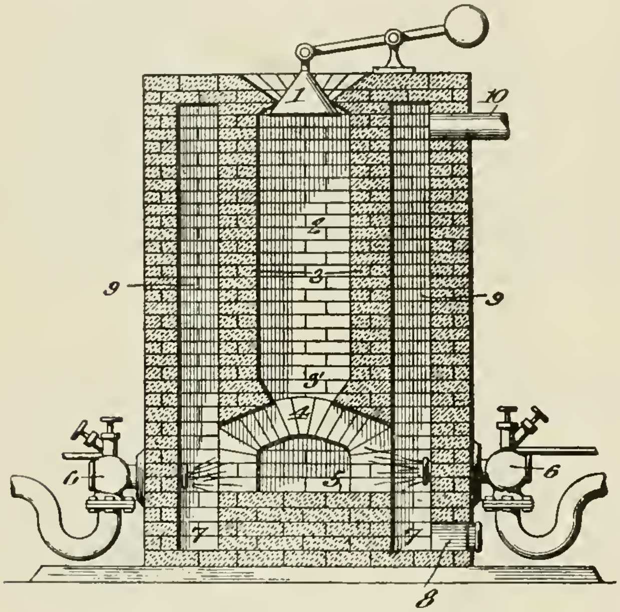

Fig. 1—Furnace Used in First Experiments

This indirect method of heating the charge proved so inefficient and entailed such a loss of heat that after several trials lasting from 18 to 24 hrs. it was abandoned as impractical, and no molten slag was obtained, although a certain amount of phosphoric acid was driven off, and a sintered product obtained in the charge chamber. The experiments showed quite clearly that in order to make the process economically practicable the full calorific power of the fuel must be utilized, which can be done only by heating the charge directly in the flame. This conclusion only served to emphasize the problem of how to maintain the reducing conditions necessary for the volatilization of the phosphoric acid, when the maximum efficiency of the crude oil flame, or that of any other fuel, can only be obtained under oxidizing conditions. Moreover, the phosphates with which the experiments were being conducted are of such a character that it is impossible to handle them in a plant of the blast furnace type, as a flame cannot be forced through a mass of such finely divided material.

At the suggestion of Professor Whitney, chief of this Bureau, the plan of spraying the phosphatic charge into the furnace along with the fuel was then tried; one oil burner was entirely cut off and a concave baffle of carborundum brick built opposite the other burner. The charge was placed in a hopper from which it was mechanically fed through a screw conveyor and blown into the furnace against the baffle in a spray under an air pressure of 30 lbs. to the square inch. It was found that if the charge was fed into the furnace very slowly a certain amount of slag low in phosphoric acid formed upon and ran down the wall of the baffle, but the vast bulk of the material, owing to its finely divided condition, was carried out of the furnace along with the gases of combustion and lost. After several trials with material of various degrees of fineness this method was also abandoned.

BRIQUETTING THE PHOSPHATE CHARGE

It was then thought that perhaps the nodulizing or briquetting of the phosphate charge might present a solution of the problem, and experiments were begun on the briquetting of mixtures of finely ground pebble phosphate, sand and coke, using various binders such as solutions of magnesium chloride, calcium chloride, calcium sulfate, sodium chloride, sodium silicate, phosphoric acid, and an acid sludge from the refining of petroleum. Short cylindrical briquettes 1 in. thick and 1 in. in diameter were made in a mold under a pressure of about 1 ton, but none of the binders employed proved satisfactory since the briquettes (either air dried or oven dried) shattered when dropped upon a stone table from a height of 1 to 3 ft. In the Florida hard-rock regions, however, the phosphate deposits in their natural state contain much soft phosphate and clay-like material of considerable plasticity, and it was thought that possibly the binding qualities of this mine-run phosphate might prove sufficiently effective without the addition of any other ingredient.

Table II—Mechanical Analysis of Finely Ground Florida Pebble Phosphate, Mine-Run Phosphate, and Furnace Charges Made up from These Phosphates

Materials Analyzed	Percentage of Various Sized Particles in Samples					
	Fine Gravel and Coarse Sand Diam. 2–0.5 Mm.	Medium Sand Diam. 0.5–0.25 Mm.	Fine Sand Diam. 25–1.1 Mm.	Very Fine Sand Diam. 1–0.05 Mm.	Silt Diam. 0.05–0.005 Mm.	Clay Diam. 0.005–0.000 Mm.
1—Florida pebble phosphate (finely ground)..........	0.0	0.0	20.4	24.8	36.0	18.8
2—Mine-run phosphate from hard rock regions......	0.0	0.2	30.2	14.6	21.0	34.0
3—Sample 1 mixed with finely ground silica and coke....	3.2	6.4	36.6	20.2	27.6	6.2
4—Sample 2 mixed with finely ground silica and coke....	0.4	0.6	35.0	18.9	19.5	25.5

In order to compare the fineness of the washed and ground pebble phosphate with that of the mine-run phosphate, samples of each were ground in a ball mill and then submitted to the mechanical analysis employed in this Bureau in connection with the classification of soil types. Samples of these two phosphates mixed with the proper proportions of finely ground sand and coke to produce a charge suitable for furnace treatment were also analyzed in the same way. For results of these mechanical analyses see Table II.

This table will show that the percentage of clay particles present (upon which the plasticity of the material largely depends) was nearly twice as great in the mine-run phosphate as in the sample of pebble phosphate, even after the two materials had been ground for several hours in a ball mill and passed through a 60-mesh sieve.

Experiments were then undertaken in briquetting samples of the original mixture except that the finely ground pebble phosphate was replaced in part and finally wholly by the mine-run phosphate. These charges in each case were mixed with 10 per cent of water and made into short cylindrical briquettes (1 in. in diameter) under a pressure of one ton.

The results of these tests[1] are given in Table III.

TABLE III—SHATTER TESTS ON BRIQUETTES

Ratio between the Two Phosphates in Charge, Per Cent		Height at Which the Briquette Shattered, Feet	
Pebble Phosphate	Mine-Run Phosphate	Air Dried Briquette	Oven Dried Briquette
100.0	0.0	3	3
90.0	10.0	3	3
75.0	25.0	4	4
50.0	50.0	4	6
25.0	75.0	6	7
0.0	100.0	9	10

It is evident that a charge containing from 20 to 25 per cent of finely divided material classed as clay can be formed into very satisfactory briquettes, but it was decided that the size of those used in the first tests was somewhat small for furnace treatment, so a larger mold was made and a round briquette 2 in. in diameter used in the next furnace experiment. The tediousness of preparing a sufficient number for a protracted run, coupled with a desire to test thoroughly the efficiency of the natural binder, prompted the writers to make arrangements with the Lehigh Coal and Navigation Co., of Lansford, Pa., to use their coal briquetting machinery on this phosphate mixture. This company kindly consented to turn over their briquetting plant for the experiment, and accordingly a half ton of the mixture was crushed to pass a 10-mesh screen, thoroughly mixed with 10 per cent of water and shipped to Lansford in air-tight barrels. Without any further treatment it was charged into a screw conveyor and fed directly to the hopper above a press of the Belgian Roll type. Very satisfactory briquettes in the shape of eggets (2.25 x 2' x 1.5) were produced which on drying withstood a drop of 6 ft. upon a cement floor without shattering.[2]

DIRECT HEATING OF BRIQUETTED CHARGE

The furnace was then so modified that a portion of the flames and hot gases of combustion from the oil burners would play up through the central shaft and thus heat the charge of briquettes directly. The burners were lighted at 8 A. M. and run steadily until 6 P. M., when a reading with an optical pyrometer was made which showed a temperature of over 1300° C. on the hearth. A few lumps of coke were then dumped into the shaft followed by 32 lbs. of briquettes. Within 10 min. fumes of phosphoric acid began to be evolved, and this continued for over an hour. At 7.45 P. M. a few more lumps of coke were added followed by 32 lbs. of briquettes. Copious fumes were evolved about 15 min. later which gradually grew less dense until at 8.50 P. M. (one hour later) another charge of 34 lbs. was added. This was followed by a fourth charge of 33 lbs. at 9.03 P. M. The heat was continued until 12:00 midnight when the optical pyrometer gave a reading of 1470° C. on the hearth. The burners were then shut off and an attempt made to tap the furnace, without success, due to the viscous nature of the slag produced.

After the furnace had cooled down, the slag was dug out and its phosphoric acid content determined. An average sample of the slag showed 11.52 per cent P_2O_5 while that which was more glassy and better fused contained only 3.53 per cent of P_2O_5. It was found that some of the briquettes which had not been fused were covered with a thin white glaze. This glaze evidently protects the carbon in the mass from the oxidizing gases until fusion takes place, for upon breaking the briquettes the coke was found unaltered, although they had been in the furnace several hours.

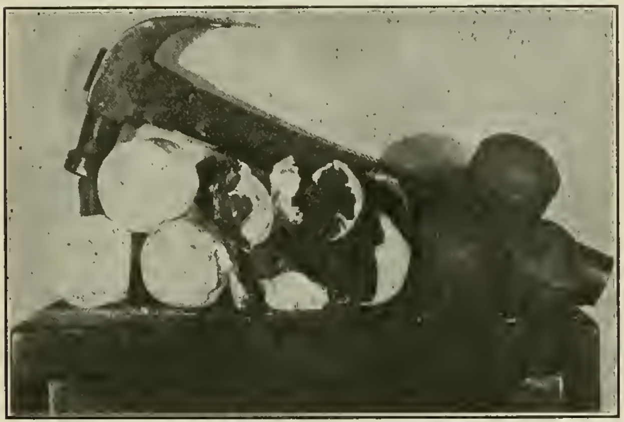

FIG. 2—EFFECT OF THE DIRECT OIL FLAME UPON PHOSPHATIC BRIQUETTES JUST BEFORE FUSION TAKES PLACE. NOTE THE UNALTERED COKE CONTAINED WITHIN THE MASS

The effect of this direct heating on the briquettes before they are actually fused can be seen in Fig. 2. On the right are the briquettes as they appear before being charged to the furnace, and at the left of the picture are shown those which have been exposed to a high temperature for several hours but not sufficiently high to cause them to melt. In the center are shown some of these latter briquettes broken open. It will be noted that there is a sharp line of demarkation between the thin glaze of the oxidized exterior of the briquettes and the interior containing the unaltered coke.

It was unfortunate that the furnace used was of such a type as to be ill adapted to the change from the indirect to the direct method of heating the charge. This fact accounts in part for the long time required in attaining a smelting temperature. With a view to overcoming this difficulty, firebrick "annexes" were built on each end of the furnace and the burners thus placed further from the charge chamber so that the oil would have a better chance for combustion. The iron plates holding the burners were replaced by cast iron water jackets to avoid the danger of injuring the burners, and a coil of pipe imbedded in a coke fire was also placed between the blower or fan and the furnace so that the air required for the combustion of the oil could be preheated before it was delivered to the burners.

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[1] These early briquetting experiments were made by Mr. L. A. Steinkoenig, who has since resigned from the Department of Agriculture.

[2] The writers wish also to express their appreciation of the courtesy extended by the General Briquetting Co., of New York City. This company not only made a number of experiments in briquetting the phosphate charge but also briquetted a ton of material used in later experiments.

The first test (No. 2, Table IV) made with these changes in the furnace was unsuccessful due to the cracking of the cast iron water jacket around one of the burners which made it necessary to close down after a few hours' run. But the second run (No. 3, Table IV) was very encouraging, since phosphoric acid was copiously evolved but the temperature attained was not quite high enough. The third test (No. 4, Table IV) was more successful while it lasted, but during the last hour of the experiment the charge chamber collapsed and the burners had to be shut off before the last of the charge was fully smelted.

TABLE IV—RESULTS OBTAINED IN SMELTING BRIQUETTES MADE OF MINE-RUN PHOSPHATE, SAND AND COKE IN A SHAFT FURNACE HEATED BY CRUDE OIL

Test	Briquettes Charged Lbs.	Time after First Charge, Hrs.	Temp Air to Oil Burner, ° C.	Temp. Attained in Furnace, ° C.	P_2O_5 in briquettes Per Cent	P_2O_5 in Slag Per Cent	P_2O_5 Volatilized, Per Cent of Total
1	153	6.5	15	Over 1400	20.46	11.52[1]	49.12
						3.53[2]	85.82
2	97	1	100 to 150	Approx. 1400	20.46	11.36	50.19
3	110	6	200 to 270	1500	20.46	11.09[1]	51.51
						10.66[2]	53.56
4	105	3.5	250 to 300	1500	20.46	8.64[1]	63.24
						1.63[3]	93.55

[1] Bulk of slag.

[2] Evidently better fused slag.

[3] Part of this slag was left in the furnace from the previous test and its phosphoric acid content further reduced by the last heating of the furnace.

While it was only in the last run of the furnace that a slag was obtained nearly free from phosphoric acid, it appeared evident that by exposing the charge to a high temperature for a sufficient length of time nearly complete evolution of phosphoric acid could be brought about.

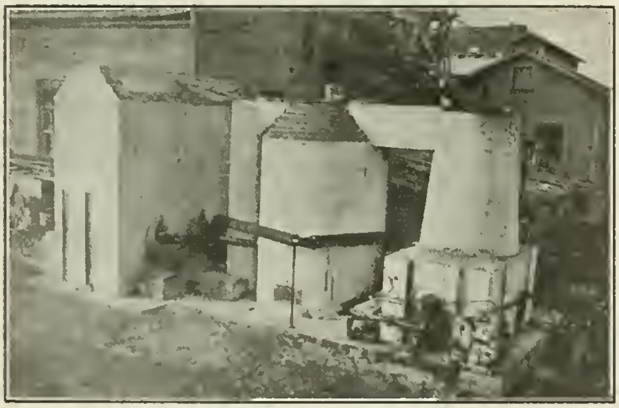

FIG. 3—NEW OIL BURNING FURNACE WITH AUXILIARY APPARATUS

The erection of a furnace better adapted for the treatment of the material and for the more efficient utilization of the heat of the burners was then begun. Auxiliary apparatus for burning of any combustible gas evolved and heating of the air to the burners by waste gases was constructed, and the whole system connected with a Cottrell precipitator for the collection of the volatilized phosphoric acid. This furnace (shown in Fig. 3) holding 700 lbs. of charge was completed early in January 1920, but adverse weather conditions and certain necessary changes in the equipment have delayed its running. Only one short test has been made so far, and the breaking of the belt to one of the motors made it necessary to cut off the burners before the experiment was completed. The results obtained in this short run, however, have convinced the workers that the form of the furnace is well adapted for the purpose and the principle used apparently sound. It is expected that interesting and valuable data will be obtained within the next few months which will show the commercial practicability of this process.

ECONOMIC CONSIDERATIONS

It is too early yet to prophesy the cost of producing phosphoric acid from mine-run phosphates by this new process, or to compare this method with that long in use for manufacturing soluble phosphates for fertilizer purposes. Certain advantages of this new process over the old sulfuric acid method, however, are so evident that they hardly need pointing out. For example, only high-grade phosphate rock containing a maximum of 4 or 5 per cent iron and aluminum oxides are at present used by the fertilizer manufacturers in producing acid phosphate. In order to obtain rock of this grade in Florida an elaborate washing and screening process is employed. This combined washing and screening process entails great losses of finely divided phosphate material which is discharged along with the impurities contained in the phosphate beds. The losses of phosphate thus entailed are fully twice as great as the quantity marketed and although much work and considerable money has been spent upon the problem, no mechanical or chemical method has yet been devised which will separate the phosphate from these impurities. It appears peculiarly fortunate that much of the material in the hard rock regions of Florida as it occurs in the mines has a composition almost ideally fitted for this furnace treatment. Instead of requiring reinforcement or enrichment by the addition of higher grade phosphate much of it must be brought to the desired composition by the addition of silica or sand, of which there is an unlimited supply at hand throughout the phosphate area. It will be seen, therefore, that the saving which can be effected by cutting out the expensive washing and screening plants, coupled with the advantage of prolonging the life of the phosphate deposits, will go far towards offsetting the additional expense, if any, involved in the preparation of the briquettes and the use of oil fuel rather than sulfuric acid as a reagent to convert the phosphoric acid into a soluble or available condition. Moreover, the product obtained is so concentrated that it can stand the expense of much longer shipments than the ordinary acid phosphate (which contains at best only from 16 to 18 per cent of soluble phosphoric acid) and by combining this concentrated phosphoric acid with ammonia and potash, fertilizers of the highest grade can be produced.

INVESTIGATIONS ON ZIRCONIUM[1]

By J. W. Marden and M. N. Rich
U. S. Bureau of Mines, Golden, Colorado

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I—PREPARATION OF ZIRCONIUM OXIDE

In the past two years much interest has been shown in zirconia as a refractory and in zirconium alloys. The demand for purified zirconium oxide has exceeded the very limited production. The following material is an abstract of a portion of a report[2] submitted on this subject.

Although there is some supply of zircon sand to be had in this country, most of the experimental work recorded below has been done on the Brazilian ore (zirkite). The American zircon sand is relatively impure (40 to 60 per cent ZrO_2), and is much more difficult to get into solution than the Brazilian ore which consists of a mixture of zircon ($ZrSiO_4$) and baddeleyite (ZrO_2), having about 73 to 75 per cent ZrO_2.[3]

The following methods have been employed in decomposing zirconium ores:

1—Fusion with $NaHSO_4$, commercial niter cake, etc.[4]

2—Fusion with caustic soda or soda ash together with sodium peroxide.[5]

3—Fusion with $NaHF_2$ or treatment with hydrofluoric acid.[6]

4—Ignition with charcoal and subsequent chloridizing.[7]

5—Electric arc fusions of zircon, CaO and carbon, leaching with water and chloridizing of the residue.[8]

TABLE I—EFFICIENCIES OF VARIOUS FUSION AGENTS ON ZIRKITE

Fusion Mixture	Ratio of Fusion Mixture to Ore	Time of Fusion	Per cent Decomposed
Na_2CO_3 KNO_3	$\left.\begin{matrix}5\\1\end{matrix}\right\} : 1$	1 hr. Clear liquid fusion	50
Conc. H_2SO_4, 180°–90° C.	10 : 1	Digested 0.5 hr.	15
Conc. H_2SO_4, boiling	4 : 1	Digested 5 hrs. and heated to dryness	80
Conc. HF	10 : 1	Boiled to dryness twice	70
$Na_2S_2O_7$	10 : 1	1 hr. Clear liquid fusion	60 Incomplete
NaOH Na_2O_2	$\left.\begin{matrix}3\\1\end{matrix}\right\} : 1$	20 min. Clear fusion	100
NaCl	10 : 1	1 hr. Clear fusion	Very Incomplete
Na_2CO_3 NaOH	$\left.\begin{matrix}1\\2\end{matrix}\right\} : 1$	0.5 hr. Clear fusion	90
Na_2CO_3 NaOH	$\left.\begin{matrix}1\\2\end{matrix}\right\} : 1$	1 hr. Clear fusion	100
Na_2CO_3 $Na_2B_4O_7.10H_2O$ (borax)	$\left.\begin{matrix}4\\1\end{matrix}\right\} : 1$	High temperature and continued fusion necessary for complete decomposition	...
NaF	5 : 1	0.5 hr.	100

After the ore is decomposed (with one exception) the zirconium is brought into solution and the hydroxide precipitated and converted into the oxide by ignition. The oxide is further purified by dissolving in acids and reprecipitating, or by recrystallization of a salt such as the oxychloride. Many trials of these methods were made on quantities of ore varying from one gram up to 10 lbs. (See Table I.)

These trials were made on small samples. On larger samples a longer time of fusion was necessary and in some cases stirring hastened decomposition.

On a commercial scale, the use of fluorides and saltpeter is expensive. The treatment of the ore with lime and coke and subsequent treatment with chlorine was attended with poor results, due partly to the small amounts of zirconium made soluble and partly to the difficulty of finding apparatus which would withstand the chlorine at the high temperature required for satisfactory chlorination.

The results of several trials in which zirkite ore has been fused and ZrO_2 subsequently produced with some success are described below.

(1) CAUSTIC SODA, SODA ASH FUSION AND PRECIPITATION WITH SO_2—One pound of zirkite (100 mesh) was sifted into a thoroughly fused mixture of 3 parts of Na_2CO_3 and 3 parts of NaOH. The fusion was continued for 1 hr., the mass cooled, crushed, and lixiviated three times with hot water. The filtered, washed residue was digested with 1 : 1 HCl, the solution filtered and diluted. The acid was neutralized as nearly as possible with soda ash without incurring precipitation and SO_2 passed into the hot solution. The precipitate yielded 0.5 lb. of nearly white oxide containing 98 per cent ZrO_2, about 70 per cent of the theoretical quantity. The total cost for this production, exclusive of labor and equipment, is about forty cents a pound.

(2) PHOSPHATE METHOD OF PRODUCTION OF ZrO_2—Ten pounds of niter cake were fused and one pound of zirkite (100 mesh) was sifted into the liquid melt. The fusion was continued for 1 hr., the mass cooled, crushed, and extracted with hot water. The liquid was filtered, some sodium peroxide and a small calculated excess of sodium phosphate added. The zirconium phosphate was filtered in a filter press, dried, and fused with 3 parts of caustic soda, crushed, leached with water, filtered, and the residue treated with diluted HCl to remove the iron and aluminum. The residue was dried and ignited. It gave a white oxide of 98 per cent purity at a cost of about forty cents a pound. A 60 per cent yield was realized.

(3) BASIC SULFATE METHOD—One pound or a larger quantity of ore was slowly heated with four parts of concentrated H_2SO_4 until free of fumes and the temperature gradually raised to 650° C. After cooling the flour-like residue was extracted with 50 parts of cold water, filtered, and sodium carbonate added to neutralize any free acid until the zirconium hydroxide just began to form. The solution was allowed to stand for 3 or 4 days, during which time the basic sulfate $4ZrO_2.3SO_3.14H_2O$ gradually separated out. When this was ignited a very high-grade ZrO_2 was obtained, which in one case contained 99.84 per cent ZrO_2 and was free from any determinable trace of SiO_2. Exclusive of labor and equipment the cost for the production

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[1] Published by permission of the Director of the Bureau of Mines.

[2] The full report will be published by the U. S. Bureau of Mines in the near future. Thanks are due to Dr. R. B. Moore and Dr. S. C. Lind for their aid and advice during this work.

[3] For a discussion of the mining and concentration of the Brazilian ore see Meyer, *Foote Mineral Notes*, November 29, 1916.

[4] Franz, *Ber.*, **3** (1870), 58.

[5] Berzelius, *Ann. Mines*, [1] **12** (1826), 297; Schiotz ("Suggested Use of Na_2O_2 for Analytical Work"), *Tidskrift. Kem. Farm. Terapi*, **14** (1917), 256.

[6] Rose, *Ann. chim. phys.*, [3] **60** (1860), 260; Marignac, *Ibid.*, [3] **60** (1860), 257.

[7] Troost, *Compt. rend.*, **116** (1893), 1227, 1428; Moisson and Lengfeld, *Ibid.*, **122** (1896), 651.

[8] Troost, *Loc. cit.*

of 1 lb. of oxide by this method was about twenty cents.

(4) OXYCHLORIDE CRYSTALLIZATION METHOD—This method was tried in several cases for the purification of zirconium compounds but it was found to be both too tedious and expensive for commercial work.

II—PREPARATION OF PURE POTASSIUM FLUORZIRCONATE AND THE CRYSTALLINE ZIRCONIUM ALUMINUM ALLOYS

Before pure metal can be prepared, the principal object of the investigations, pure zirconium oxide or zirconium salts, must first be obtained. Even the oxide prepared by the basic sulfate method of crystallization contains various impurities. The quickest and most satisfactory method of purification is by means of successive crystallization of K_2ZrF_6, previously described by Marignac[1] and others.

The K_2ZrF_6 is prepared by dissolving ZrO_2 in hydrofluoric acid. This was done in the present work in lead vessels made for the purpose having a capacity of one to two gallons.

After heating, the oxide gradually dissolves and a clear solution is obtained. This is diluted and filtered (using a rubber funnel) into a clean lead dish. It should not come in contact with glass on account of the formation of fluorsilicates.

A filtered solution of C. P. potassium carbonate is added in sufficient quantity for the complete formation of all the K_2ZrF_6, but not enough to neutralize all of the free acid. If too much K_2CO_3 is added the zirconium is precipitated as the hydroxide, and more hydrofluoric acid is needed. Potassium carbonate should be used in place of potassium hydroxide because of its greater freedom from sodium salts. The sodium fluorzirconate is very insoluble and cannot be easily recrystallized.

The solubility of the potassium salt varies considerably with the temperature, as is shown from the following figures:

	G. in 100 cc. H_2O	
Temp. ° C.	K_2ZrF_6	Na_2ZrF_6
100	25.0	1.67
20	15.0	..
18	..	0.38
0	0.78	..

After cooling the hydrofluoric acid solution prepared above, the crystals of K_2ZrF_6 are filtered off. The crystals are redissolved in hot water containing a little hydrofluoric acid, filtered while hot, and allowed to cool. The crystals of K_2ZrF_6 again separate.

Starting with 98 per cent ZrO_2, three crystallizations yield a perfectly white crystalline salt which analyzed 32.10 per cent (theoretical: 32 per cent) Zr. A one-gram sample did not contain enough of either iron or titanium to give distinguishable colorimetric reactions after the fluorides had been removed and the salt was considered to be of at least 99.99 per cent purity.

In the production of zirconium metal the so-called "crystalline zirconium" alloy has also been used. This alloy has often been mistaken for zirconium metal on account of its great stability toward chemical agents and oxidation. It has been prepared by the method of Weiss and Newman.[1]

Recrystallized K_2ZrF_6 is fused in a graphite dish, in a gas furnace. In this investigation bored-out graphite sticks in the shape of deep cylindrical vessels were used. A temperature of about 900° C. is necessary to get a clear liquid. When the fusion is complete 1.5 times its weight of aluminum are added, a little at a time. During these additions a vigorous reaction takes place. When the reaction is finished the heating is continued for 10 to 20 min., the whole mass covered with a layer of sodium and potassium chlorides, and allowed to cool. When the dish is broken the aluminum alloy is found collected free of salt in the bottom of the dish. Flat plate-like, apparently monoclinic, crystals are to be seen on the surface. The alloy is carefully cleaned off, broken up with a chisel and treated with strong solutions of caustic soda until no more aluminum will dissolve. The residue is separated by decantation and filtration, then boiled with successive portions of 1 : 1 hydrochloric acid to remove the zirconium hydroxide which forms.

On filtering and drying the residue it is found to consist of silver-white crystals about 0.5 to 1 mm. across, and about as resistive to chemical action as zirconium metal itself. The more silicon impurity present the larger the crystals. The following is an analysis of this material:

	Per cent
Al	30
Zr	68
Fe, Si, small amts. Ti, etc.	1.0
TOTAL	99.0

A much purer product showed the following analysis:

	Per cent
Al	29.9
Zr	70.00
Fe	0.03
Si	0.05
Ti, not enough to determine	
TOTAL	99.98

Since the K_2ZrF_6 can be prepared in very pure condition, the purity of the crystals is governed very largely by the purity of the aluminum metal used. The so-called C. P. aluminum metal rarely runs over 99.5 per cent Al, the principal impurities being iron and silicon.

This aluminide (Zr_3Al_4) may be prepared in impure condition directly from zirkite by fusing the ore with sodium fluoride and then adding the aluminum. The treatment of the alloy (with caustic soda) after cooling is as above. Following is an analysis of this product, where a part of the aluminum is replaced by silicon:

	Per cent
Al	13.10
Zr	74.47
Fe	0.84
Si	11.15
Ti, not determined	
TOTAL	99.76

A crystalline silver zirconium alloy may also be prepared by the alumino-thermic reduction.

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[1] *Loc. cit.*

[1] *Z. anorg. Chem.*, **65** (1910). 248.

III—PREPARATION OF ZIRCONIUM METAL

The literature refers to four varieties of zirconium metal: amorphous, crystalline, graphitoidal, and sintered. The properties given for these varieties of metal by various authors differ widely. The historical references have been omitted for the most part for the sake of brevity.

The following methods have been employed for the production of this metal:

A. AMORPHOUS—(1) Reduction of K_2ZrF_6 with sodium metal in an iron tube;[1] (2) Passing $ZrCl_4$ over heated sodium metal;[2] (3) Reduction of ZrO_2 with calcium metal.[3]

B. CRYSTALLINE[4]—Reduction of K_2ZrF_6 with large excess aluminum metal in a graphite dish. This so-called crystalline zirconium has been shown to be an alloy of aluminum and zirconium.

C. GRAPHITOIDAL—The interaction of sodium zirconate and iron is said to yield this variety[6] of the metal. After repeated failures in attempting to prepare it the conclusion is drawn that there is no such variety.

D. SINTERED[6]—In most cases the authors have introduced the word "coherent" for this variety of metal.

1—Alumino-thermic reductions produce coherent metal.

2—Heating the amorphous product obtained in A–3 yields small lumps or granules of partly coherent metal.

3—Reduction of ZrO_2 with carbon yields Zr metal mixed with carbide.

In the experimental work, all of these methods have been tried in the production of the amorphous and coherent varieties of zirconium.

The amorphous metal has been prepared by the following methods:

1—Reduction of K_2ZrF_6 in an evacuated iron tube with a small excess of sodium. This takes place on heating the tube to a dull red heat. The mass is cooled and extracted with dilute hydrochloric acid until all the salts are removed. Samples were prepared containing 98 per cent zirconium.

2—Reduction of K_2ZrF_6 with aluminum in the Arsem vacuum furnace, in which the excess salts were distilled away, yielded a good grade of amorphous zirconium contaminated with some aluminum.

3—Reduction of ZrO_2 with aluminum will under certain conditions yield an impure amorphous metal.

PROPERTIES OF AMORPHOUS ZIRCONIUM

PHYSICAL

Atomic weight: 90.6 (taken from literature).

Alloys: With one exception does not form alloys under ordinary conditions. Can be alloyed by heating with aluminum. Does not form amalgams.

Boiling point: Very high.

Corrosion: Remains unchanged at ordinary temperatures although when suspended in water it apparently reacts slowly to form the hydroxide.

Color: Black; heated above 1000° C. gray, metallic.

Electrical conductivity: Very low: black amorphous nonconductor.

Fusibility: According to Wedekind, it partly sinters at 1000° C. although we have never observed fusion at any such low temperature. The material apparently runs together to form the white coherent metal, looking like iron steel, a little above 1600° in a high vacuum in an atmosphere of exceedingly dry and pure hydrogen. If a small amount of air or oxygen is present, this fusion does not take place. The melting point of the zirconium is in the neighborhood of 1600°. When heated to 1000° C. the amorphous black metal changes to gray-colored material, taking a metallic polish.

Hardness: Soft, velvety. Ignited above 1000° C. granular.

Luster: Metallic when polished. When pressed into sticks at a high pressure and polished it has the appearance of a solid gray metal.

Melting point: About 1600° C.

Occlusion of gases: This material absorbs or occludes gases very readily. It also seems to have much affinity for moisture.

Specific gravity: About 4.0. The specific gravity varies with the amount of heating. The amorphous metal when heated in the high vacuum furnace gradually shrinks and the specific gravity increases until coherent metal is obtained, which has a specific gravity of more than 6.0. The amorphous metal as ordinarily prepared has a specific gravity of about 4.0.

Volatility: Does not volatilize at 2000° C. in a vacuum of 1 to 2 mm.

CHEMICAL

Combines readily with chlorine at low red heat; in nitrogen it burns to nitride at dull red heat. When heated in the air to a dull red heat, it burns to the oxide with a white incandescence. It is readily soluble in hydrofluoric acid even when dilute. It is slowly soluble in 1 : 1 hydrochloric acid. It is slowly soluble in nitric acid but more readily soluble in sulfuric acid. It dissolves in the ordinary fusion agents such as potassium bisulfate, caustic soda, etc. Amorphous zirconium formed by the reduction of K_2ZrF_6 with sodium will dissolve in water, forming bluish colloidal solutions which readily pass through the filter paper.

The coherent metal was prepared alumino-thermically in small beads which showed the following analyses:

	Per cent	
Zr	99.40	99.50
Ti	0.45	0.40
Fe	0.01	0.02
Al and Si, by difference	0.14	0.08
TOTAL	100.00	100.00

A typical charge for this alumino-thermic reduction was made as follows:

ZrO_2	90 g.
$KClO_3$	30 g.
Al	40 g.

All the materials were first purified, thoroughly mixed and finally fired in a fire-clay crucible.

The coherent metal was also prepared in the Arsem furnace in an evacuated atmosphere of very pure, very dry hydrogen by the reduction of K_2ZrF_6 with aluminum. This method is that used in the reduction to the amorphous, but this amorphous metal cannot be made to cohere unless the evacuated atmosphere in the furnace is entirely free from moisture and air. The following is an analysis of this metal:

	Per cent
Fe and Si	0.2
Al	Absent
Zr	99.5
TOTAL	99.7

Coherent metal was also prepared by arcing pressed sticks of the crystalline zirconium-aluminum alloy in an evacuated atmosphere of hydrogen.

PROPERTIES OF COHERENT ZIRCONIUM

PHYSICAL

Alloys: Does not dissolve in lead, tin, or silver by simply heating above the melting point of the respective metal.

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[1] Berzelius, *Ann. Phys. Chem.* (Pogg.), **4** (1825), 124; 8 (1826), 186.

[2] Troost, *Compt. rend.*, **61** (1865), 109.

[3] Wedekind, *Ann.*, **395** (1913), 149.

[4] Weiss and Newman, *Z. anorg. Chem.*, **65** (1910), 248; *Am. J. Sci.*, [4] **29**, 457; *J. Soc. Chem. Ind.*, **29**, 218.

[5] Troost, *Loc. cit.*

[6] Kuzel and Wedekind, U. S. Patent 1,088,909 (1914).

Will alloy with silver, aluminum, and iron when heated above the melting point of zirconium in the Arsem furnace. Alloys of silver, iron, nickel, or aluminum are easily made by simultaneous reductions at high temperatures (Goldschmidt's process). Does not form amalgams.

Corrosion: Does not rust or tarnish on long standing in the laboratory but when polished remains bright white like polished nickel.

Color: White metallic.

Electrical conductivity: Fairly good conductor. Probably less than that of iron.

Fusibility: Can be readily fused under the proper conditions away from the air at about 1600° C.

Hardness: About 6–7 on the Mohs scale. The hardness varies with the method of preparation and purity of samples. The pure samples were less hard than the more impure metal. In all cases the metal would readily scratch glass. As would be expected with a metal of this degree of hardness it is also quite brittle and can easily be broken by lightly pounding with a small hammer. The metal is still very hard although less brittle at a red heat. The hardness on the Shore scleroscope is 40 to 45.

Luster: White metallic. Takes a fine polish like nickel.

Melting point: About 1600° C. The U. S. Bureau of Standards has found the melting point of the metal from 1400° to 2200° C. as it was prepared by various authors. In recent trials the metal prepared appears to melt very close to 1600° C. in an atmosphere of pure dry hydrogen.

Occlusion of gases: When samples of zirconium are fused in pure dry hydrogen and rapidly cooled, a phenomenon similar to the so-called "spitting" of silver is observed. When silver is fused it dissolves oxygen and on cooling the oxygen is evolved, causing the "spitting" and leaving the metallic mass porous. The zirconium, when similarly treated in hydrogen, shows the same porous appearance. This porosity is not observed in samples prepared by the Goldschmidt process.

Specific Gravity: Partially sintered amorphous zirconium shows a specific gravity of 4.39. The specific gravity of the alumino-thermic, 99.5 per cent zirconium is 5.55, while the specific gravity of 99.5 per cent coherent metal prepared by the reduction of K_2ZrF_6 with aluminum was found to be 6.06. The specific gravity of zirconium, as with other metals, varies with the method of treatment.

CHEMICAL

The white metal is much less chemically active than the amorphous metal. It does not react with chemical reagents readily at ordinary temperatures. This variety of the metal in a solid piece can be heated to a bright red heat in the blast flame with no more than a very thin bluish superficial surface oxidation. It can be burned in the air by heating to a white heat in the finely divided condition. It is insoluble in all acids except aqua regia and hydrofluoric acid. The metal dissolves easily in hydrofluoric acid (1 : 1) but it takes at least 5 hrs. to dissolve one gram of the solid metal by digesting in an excess of aqua regia. The metal is not readily dissolved by fusion with bisulfates, caustic soda, etc.

IV—COMPARISON OF THE METHODS OF ANALYSIS

On attempting the analysis of zirconium ores by the different methods in the literature very conflicting results were obtained. For example, a sample of zirkite ore gave the following percentages of ZrO_2 by different methods:

TABLE II—ANALYSIS OF ZIRKITE ORE BY DIFFERENT METHODS

Method Employed	Weight of Ore (or Aliquot) G.	Weight of Phosphate G.	Weight of ZrO_2 G.	ZrO_2 Per cent
Phosphate	0.0853	0.1215	0.0626	73.3
	0.0707	0.1010	0.0520	73.5
Sodium thiosulfate	0.2000	....	0.1740	87.0
	0.2000	....	0.1700	85.0
Sodium iodate	0.2000	....	0.0947	47.35

The results obtained by the phosphate method are very nearly the correct ones but an inexperienced worker would have trouble in deciding just what percentage of ZrO_2 the ore should have. The thiosulfate precipitate is high, due to occlusion of large amounts of sodium salts, while the iodate results are low due to too strong acidity of the solution for precipitation.

The following methods in more common use are listed and comparisons are made as to their relative merits. The more important methods for the estimation of zirconium are as follows.

1—The phosphate precipitation. Hillebrand, U. S. Geol. Survey, *Bull.* **73** (1900); Lundell and Knowles, *J. Am. Chem. Soc.*, **41** (1919), 1801; Nicolardot and Reglade, *Compt. rend.*, **168** (1919), 348.

2—The thiosulfate or SO_2 precipitation. Baskerville, *J. Am. Chem. Soc.*, **16** (1894), 475; Ferguson, *Eng. Min. J.*, **106** (1918), 356, 793.

3—The iodate separation. Davis, *Am. Chem. J.*, **11** (1889), 25.

4—The peroxide precipitation. Bailey, *J. Chem. Soc.*, **149** (1886), 481; Walker, *J. Am. Chem. Soc.*, **20** (1898), 513.

5—The phenylhydrazine precipitation. Allen, *J. Am. Chem. Soc.*, **25** (1903), 421.

6—The cupferron precipitation. Ferrari, *Atti ist. Venata Scienze Lettere ed arti*, **73** (1914), 445; Brown, *J. Am. Chem. Soc.*, **39** (1917), 2358.

7—The fluoride separation. Headden, *Proc. Colo. Sci. Soc.*, **11** (1917), 185.

In a study of these methods it was found that the fluoride separation is incomplete and the peroxide precipitation takes place only when the concentration of the peroxide is very high in the solution. Methods 4 and 7 were therefore given but scant attention.

TABLE III—COMPARISON OF RESULTS BY DIFFERENT METHODS

Weight of ZrO_2 Taken Grams	Weight of ZrO_2 Found	Variation
Phosphate Method:		
0.0865 ZrO_2	0.0875	
0.0357 Fe_2O_3	0.0877	+0.0011
0.0471 Al_2O_3		
	Av., 0.0876	
Sodium Thiosulfate Method:		
0.0865 ZrO_2	0.0845	—0.0018
No Fe_2O_3 or Al_2O_3	0.0850	
	Av., 0.0847	
0.0865 ZrO_2	0.0988	No check; large amts. iron and alum in precipitate
0.0643 Al_2O_3	0.1873	
0.1514 Fe_2O_3		
Phenylhydrazine Method:		
0.0865 ZrO_2	0.1370	ZrO_2, 0.0865
0.0357 Fe_2O_3	0.1388	Al_2O_3, 0.0471
0.0471 Al_2O_3		
	Av., 0.1380	0.1336 + 0.0044
Cupferron Method:		
0.0865 ZrO_2	0.1213	ZrO_2, 0.0865
0.0357 Fe_2O_3	0.1219	Fe_2O_3, 0.0357
0.0471 Al_2O_3	0.1213	0.1222 — 0.0007
	Av., 0.1215	

The phosphate is best precipitated from about 10 per cent sulfuric acid to which H_2O_2 is added to retain the titanium in solution. An excess of disodium phosphate should be used, the solution heated to boiling and allowed to stand, before filtration. Due to the gelatinous nature of the precipitate and difficulties in washing no larger quantity than 0.05 to 0.1 g. of ZrO_2 should be precipitated from 200 cc. of solution at one time.

It has been found from Table III and similar tables that:

(1) The phosphate gives fairly good results in the presence of iron and aluminum but a 50 per cent excess of ammonium phosphate should be used when the acidity lies between 10 and 20 per cent H_2SO_4.

(2) The sodium thiosulfate method cannot be used in the presence of much iron and aluminum salts.

(3) Phenylhydrazine precipitates the zirconium together with the aluminum, away from the iron, but this precipitate is slimy and difficult to wash free of impurities. The results by this method should equal the weight of ZrO_2 + the weight Al_2O_3 but are too high *for this reason.* If done in dilute solution the phenylhydrazine separates the Zr and Al from the iron.

(4) Cupferron serves to separate Zr and Fe from aluminum with a fair degree of exactness. The cupferron precipitate is a desirable one to handle.

(5) Although not shown here, the sodium iodate method can be used with accuracy in carefully neutralized solutions. It is subject, however, to somewhat the same limitations as the sodium thiosulfate method.

A method of analysis for zirconium which could be applied to alloys must be such as to include separation from Fe, Al, V, Cr, Ni, Co, Ti, Si(?), and perhaps other elements. The method of analysis of ores is not complicated, as elements such as V, Cr, Ni, and Co are not usually found in zircon ores.

RECOMMENDED METHOD OF ANALYSIS

PREPARATION OF SAMPLE—The alloys, which are for the most part brittle, are pulverized as far as possible in a steel mortar, while the ores are pulverized to pass a 100- to 200-mesh sieve before analysis is undertaken. The thorough grinding of samples of the ore is very important as much of the ease with which the samples go into solution in various fusion agents depends on the fineness of subdivision of the sample.

METHOD OF SOLUTION AND SEPARATION OF THE SILICA—Alloys should be dissolved in aqua regia using about 0.5 to 1 g. of the alloy and, after the solution has been made, diluting it up to 500 cc. or a liter so that a suitable aliquot of 100 cc. would represent about 0.05 g. of ZrO_2 for analysis.

If the percentage of zirconium and silicon in the alloy is high, the process of dissolving it in aqua regia will be slow. It is occasionally necessary to use hydrofluoric acid in a platinum dish in preparing the solution. The use of this is objectionable when the percentage of silicon is desired and the following procedure is to be preferred:

After treatment with aqua regia and evaporating the solution nearly to dryness to separate the silica, if there is an insoluble residue other than silica remaining, the solution is diluted, filtered, and the residue ignited in a platinum crucible. This is then fused with sodium or potassium bisulfate, the fused mass cooled, dissolved in water, and the insoluble silica again filtered and washed. The filtrate is combined with the filtrate from the aqua regia treatment in a 500-cc. volumetric flask. The silica is determined by the usual method of volatilization with HF and H_2SO_4, and if there is any weighable residue remaining after this treatment, this must be brought into solution by means of a second fusion with bisulfate, the solution from this fusion being combined with the other filtrates in the volumetric flask. Suitable aliquots of this solution, made up to 500 cc. and containing 5 per cent H_2SO_4, are taken for the zirconium determination. In no case should more than 0.1 g. of ZrO_2 be taken.

In the case of ores, 1 g. of the ore is fused with four parts of NaOH and one part of Na_2O_2 in a nickel crucible to a clear, dull red liquid fusion for 15 or 20 min. The fused mass is cooled and dissolved out from the crucible with warm water to make a volume of about 100 cc. The zirconium and most of the titanium are in the form of insoluble sodium zirconate and sodium titanate suspended in the solution. The solution is then made about 10 per cent acid with sulfuric acid and heated to dissolve all the zirconium and titanium. After boiling down nearly to dryness the solution is again made up to about 200 cc. and the silica filtered off, together with any insoluble residue. The filtrate is reserved in a 500 cc. volumetric flask, while the silica is determined in the residue by the customary H_2SO_4 and HF treatment. If there is a residue left after the hydrofluoric-sulfuric acid treatment this must be again fused with caustic soda and sodium peroxide and the solution obtained by the subsequent acid treatment combined with the filtrate in the volumetric flask for the analysis.

It is frequently the case that two and even three fusions are necessary in order to obtain a complete solution. It might be further suggested in the determination of the silica that the residues for this purpose be first ignited with a little sulfuric acid and weighed before the hydrofluoric acid treatment is attempted. If this is not done even where there is a small percentage of silica sometimes the weight will be found to increase instead of decrease as it should.

ANALYSIS OF SOLUTION CONTAINING Fe, Al, Cr, Ni, Mo, W, Ni, Co, Zr, Ti, AND P—The acid solution which is now free of silica and has been drawn off in a suitable aliquot to contain about 0.05 g. ZrO_2 is heated nearly to boiling (about 90° C.) and ammonium hydroxide added until a slight permanent precipitate is formed. Dilute HCl (1 : 1) is added from a burette drop by drop until the precipitate which has formed just redissolves and the solution is perfectly clear. About five drops more of the HCl are added to the solution, which should now have a volume of about 200 cc. Three cc. of phenylhydrazine which have previously been dissolved in 10 cc. of hot water are added, and the solution stirred vigorously and filtered immediately through quantitative paper. After washing thoroughly with hot water, the paper and precipitate are dried and ignited in a platinum crucible. This procedure separates practically all of the iron from the zirconium, titanium, and aluminum. In order to separate further the zirconium and titanium from the aluminum the following method is employed: Fuse the residue in the platinum crucible with 5 to 10 g. of Na_2CO_3 and one g. KNO_3; after cooling disintegrate the fused mass with hot water, filter, and wash. The residue on the paper now contains zirconium and titanium free from all interfering substances such as aluminum, vanadium, etc., with the possible exception of traces of iron. The paper containing the sodium zirconate and titanate is dried and ignited in a platinum crucible and the titanium and zirconium obtained in solution by cautiously fusing with 5 to 10 g. of $KHSO_4$, bringing the temperature up to a dull red heat for about one-half hour and using a cover on the crucible to avoid spattering during the process of fusion. The zirconium may be determined by practically any of the methods mentioned above, using this solution, provided that the quantity of zirconium in the solution is not greater than 0.1 g. calculated as ZrO_2. Most precipitates of zirconium are more or less gelatinous, bulky, and difficult to filter and wash, and therefore if larger quantities are taken, accurate results cannot be attained.

If the zirconium alone is desired and there is no need of separating the iron, aluminum, etc., from the solution, the phosphate method is the only one which gives accurate results and a clean separation from both the above-mentioned elements.

The solution which has been freed from silica, containing not over and preferably less than 0.05 g. ZrO_2, is diluted to 200 cc. volume, made 10 per cent acid with H_2SO_4, 2 cc. hydrogen peroxide added, heated nearly to boiling and a slight excess of disodium phosphate solution added. The zirconium precipitate is a white or greenish white flocculent, gelatinous precipitate. After allowing to stand for about 2 hrs. or longer the precipitate is filtered onto an 11 cm. filter paper and thoroughly washed with hot dilute sulfuric acid. The paper and contents are then transferred to a platinum crucible, ignited, and finally blasted to remove as much of the carbonaceous matter as possible. The proper ignition of this precipitate is one of the most difficult steps of the whole procedure. The weight of zirconium pyrophosphate, ZrP_2O_7, multiplied by the factor 0.4632 yields the weight of ZrO_2.

Iron is determined in the solution from the silica filtration by the method of precipitation as the sulfide from ammonium tartrate solution. This method is well known. To 100 cc. portions of the silica-free solution 0.5 g. of tartaric acid is added, the solution heated to boiling, made strongly alkaline with NH_4OH, and H_2S added. The iron precipitates as the sulfide, is filtered out, washed, and weighed as Fe_2O_3.

The titanium may also be determined on a separated portion of the original solution (if all HF or HNO_3 has been first removed) by Weller's colorimetric method with H_2O_2 or by titration with methylene blue.

Aluminum is usually determined by difference, the aluminum, zirconium and titanium being precipitated with sodium thiosulfate, SO_2, or phenylhydrazine practically free from iron, if the percentage of iron in the original is not high. In certain cases it is necessary first to remove the iron by the above-mentioned method and destroy the ammonium tartrate by the ordinary methods of wet combustion with nitric and sulfuric acids before the precipitation of the others is attempted.

V—BIBLIOGRAPHY

Before much work on zirconium was attempted, all of the methods for the production of the metal, etc., described in the literature were reviewed and tried. At the start there were many conflicting data regarding the properties and reactions of zirconium and its compounds. A complete bibliography of the subject contained about five hundred references, from some forty-one different journals.

It has been arranged in alphabetical order with regard to names of authors under the following headings:

1—Zirconium Minerals
2—Preparation, Properties, and Uses of Zirconium Salts
3—Analytical Chemistry of Zirconium
4—Zirconium Metal
5—Zirconium Alloys

The bibliography also includes references on the use of ZrO_2 as a refractory and as an opaquing agent in enamels, etc. All of the technical uses have been faithfully included. Section 5 has been devoted to the preparation and properties of zirconium alloys.

A CHEMICAL STUDY OF FROZEN FISH IN STORAGE FOR SHORT AND LONG PERIODS

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The present investigations upon fish commercially frozen and stored were undertaken in the hope of furnishing exact information upon which the public could base its opinion concerning the wholesomeness of frozen fish as food. The part of these investigations of practical interest to the trade has already been published in *Departmental Bulletin* 635 of the U. S. Department of Agriculture, and entitled "The Commercial Freezing and Storing of Fish."

The magnitude of the frozen fish industry of this country is indicated by the fact that over 120,000,000 lbs. of food fish.[1] valued at more than $12,500,000 to the wholesaler, entered cold storage in 1918. Depending upon the locality, the amount of frozen fish in storage during a year represents from 4 to 15 per cent of the annual catch.[2] Furthermore, there are over 190 fish-freezing and storage plants in the United States, and the number is increasing. These statistics show that the practical advantage and economic necessity of cold-stored fish have long been realized by those familiar with the industry. Until recently, however, no chemical investigation has been made of the effect upon the food value of the freezing and storing of fish.

HISTORICAL

In 1913 several Dutch scientists[3] made experiments with ice-chilled and frozen fish to see what changes in microscopical appearance occurred under refrigeration and what part bacteria played in the process of deterioration. This commission found that certain changes take place in the reaction of the tissues to litmus, the flesh of some species being acid, and, of some, alkaline during decomposition. Some differences in the histology of fresh and frozen fish were noted. All of this work was, however, of a preliminary nature and not in any sense an exact chemical investigation.

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[1] Estimate based on U. S. Dept. of Agriculture, Bureau of Markets, Report of Stocks of Frozen and Cured Fish, December 15, 1918; issued December 28, 1918.

[2] Hearings before the Committee on Agriculture, House of Representatives, on Cold Storage Legislation, August 14, 1919, p. 203.

[3] J. M. Bottemaine, "Notes on the Investigation of Preserving Fish by Artificial Cold." (*a*) Preliminary Report, 48 pages; (*b*) Preprint, 3 pages; 3rd International Congress of Refrigeration, 3rd Section (The Netherlands), Washington-Chicago (1913).

The quantitative chemical study of changes in fish flesh upon standing or during cold storage is a new one. The researches of Richardson and Scherubel,[1] Emmett and Grindley,[2] and others upon meat during storage opened the way in that field. Pennington[3] and Wiley, *et al*,[4] have done fundamental work on the chemistry of ripening processes in the flesh of poultry and game.

The investigations of Smith[5] and of Perlzweig and Gies[6] on chemical changes in fish during cold storage are the pioneer contributions to our knowledge of this subject. They determined the chemical composition, ammonia content, etc., of fresh fluke, *Paralithys dentatus*, and flounder, *Pseudopleuronectes americanus*, before freezing, and also made the same determinations at intervals during two years on the same lot of storage fish. These fish were all handled according to the usual trade practices, except that they were probably frozen more promptly after catching than the average commercially frozen fish. Even at the end of two years of storage these investigators were unable to detect any appreciable variations in chemical composition or nutritive value attributable to freezer storage. There were no significant changes in the percentages of the ordinary food constituents, or of ammoniacal nitrogen, acidity of fats or reaction of the aqueous extracts; all of which would tend to show that neither autolytic nor bacterial influences had been active. Furthermore, two years after storage the fish were found palatable and entirely acceptable as food.

Recently, Almy[7] investigated the chemical changes in mackerel (*Scomber scombrus*) after freezing and cold storage for 9 mo. Unlike the so-called "bottom" fish used in the researches of Smith, which contain less than one per cent of fat, mackerel are tender, oily fish, very prone to rapid deterioration unless handled carefully and kept constantly under refrigeration. This investigation represented the first attempt to study the nitrogen distribution in the flesh of frozen fish, but, as the work was a continuation of that reported in the present paper, no attempt will be made to describe the methods used but only to summarize the conclusions based on the study of a typical fat-containing fish. Almy found that during storage there were in frozen mackerel slight increases in the amount of total nitrogen and coagulable nitrogen in the aqueous extracts, but no change in the content of ammonia and amine nitrogen. There were also slight increases in the acidity of the aqueous extracts of the flesh and of the fat extracted from the flesh of the cold stored mackerel. In no case, however, was there any significant change in the food value of the fish or any evidence of deterioration at the end of 9 mo. At the end of this period of storage some of the mackerel were cooked and prepared for the table. Unlabeled portions of these cooked storage mackerel and of perfectly fresh mackerel were served to a representative group of 15 people in New York City, and none of them was able to detect any difference between the fresh and frozen fish as judged by appearance and flavor.

METHODS OF THE PRESENT INVESTIGATION

HISTORY OF FISH ANALYZED

Two species were used in the present investigation: weakfish, *Cynoscion regalis*, and bluefish, *Pomatomus saltatrix*, which is carnivorous and a voracious enemy of all fish smaller than itself. The medium sized fish of both species were studied. All of the specimens were caught off the New Jersey coast and promptly landed at the shore without any contact with ice. In all the lots but one the fish were eviscerated before they were landed. As soon as possible the different lots were weighed and carted a short distance to a fish freezer, where the specimens for freezing were washed and frozen in pans on brine pipes in the usual way. The temperature of the freezing room was —5° F., and of the storage room about 0° F. This is lower than the customary storage temperature, but the isolated nature of the plant necessitated such a practice as a safeguard to allow time for repairs in case of a break in the refrigerating machinery. The fish to be analyzed immediately in the freshly frozen condition were quickly chilled and frozen, and while still at a temperature below 0° F. were taken to the laboratory in Philadelphia where they arrived hard frozen. They were then thawed slowly by standing over night in an icebox, cleaned, and prepared at once for analysis in the laboratory. The frozen fish for long holding were shipped in cork-insulated shipping cases, and upon reaching Philadelphia were at once transferred to a storage room where a temperature of about 15° F. was maintained during the various periods of storage. Each lot was boxed in the commercial way and reglazed whenever necessary, which was about three times during a year. As indicated in the tables, some of the weakfish were not glazed. One lot was stored without removal of entrails (in the so-called "round" condition), and another lot was wrapped in commercial semi-parchment paper without any glazing. These variations from the commercial practices were made in order to study the effects of such modifications.

PREPARATION OF SAMPLES FOR ANALYSIS

The thawed fish were prepared for sampling by separating as completely as possible the edible portion from the heads, tails, skins, entrails, and bones, which were discarded. The edible part was weighed and the difference between this weight and that of the whole fish represented the refuse or inedible portion. The flesh was ground three successive times in a meat chopper, and the samples of individual fish mixed thoroughly by hand. In the case of bluefish, which were of considerable size, two specimens were used; but of the weakfish three were analyzed in each lot, the edible portions being united, ground again, and well mixed before final sampling for analysis.

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[1] THIS JOURNAL, **1** (1909), 95.

[2] *Ibid.*, **1** (1909), 413.

[3] Hearings before Committee on Manufactures, U. S. Senate, on Foods Held in Cold Storage, May 25, 1911, p. 57.

[4] U. S. Dept. of Agriculture, *Bulletin* **115** (1908).

[5] *Biochem. Bull.*, **3** (1913), 54.

[6] *Ibid.*, **3** (1913), 69.

[7] L. H. Almy, unpublished report of a study of the chemical changes occurring in frozen mackerel during storage for a year. Research performed in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Columbia University, 1917.

The following section contains a description of the various determinations of chemical changes in the fish during cold storage, and is intended to include every determination that offered any possibility of giving useful information about fish flesh and its changes. Possibly, some of these determinations are unnecessary and some may be of little value, but all should help to give information about the adequacy of the methods themselves as applied to problems of this sort. Most of the determinations have been adapted from the work of early investigators upon meat and poultry. Any new methods or modifications will be apparent to those familiar with chemical work on cold storage problems.

ANALYTICAL PROCEDURE

MOISTURE, ETHER EXTRACT, ASH AND TOTAL NITROGEN—The methods used for the estimation of the percentage of moisture, ether extract, and ash are those described in *Bulletin* 107 (revised) of the Bureau of Chemistry, U. S. Department of Agriculture. Total nitrogen was determined by the method of Kjeldahl and Gunning, using 0.1 *N* acid and alkali.

FAT-FREE SOLIDS—It is a well-recognized fact that the flesh of fat fish contains a lower per cent of moisture than that of lean fish. The reciprocal relation of the per cent of moisture and fat in the flesh of fish of the same species is such that the per cent of fat-free solids is more or less constant. An increase of 2 per cent in the fat-free solids therefore shows that the per cent of moisture has decreased by 2 per cent. The per cent of fat-free solids was computed in each case by subtracting the per cent of fat from the per cent of solids.

AMMONIA AND AMINE NITROGEN BY AËRATION—Loosely bound basic nitrogen compounds, which in fish flesh include ammonia and amine nitrogen, were estimated by a modification of the Steel-Gies method described by the authors.[1]

TOTAL SOLUBLE NITROGEN AND COAGULABLE NITROGEN—The extraction of the flesh and the determinations of soluble nitrogen and coagulable nitrogen were made by the methods previously outlined.[1]

SOLIDS—One hundred cc. portions of the water extract of the flesh were evaporated on the steam bath in weighed platinum dishes, the residue being dried at 100° C. to constant weight.

ASH—The organic matter of the soluble solids was burned off in a muffle at low red heat to avoid any loss of chlorides.

ORGANIC EXTRACTIVES—This is the difference between ash and solids already determined.

ACIDITY OF THE EXTRACTS—Owing to the presence of both proteins and phosphates in extracts of fish flesh, it is not believed that direct titrations of acidity can give results of absolute value. For comparative studies in investigations of this sort, however, such direct titrations would certainly show any significant increases in acidity due to changes occurring during a prolonged period of storage. Correction was made for the very slight acidity of the distilled water used in preparing the extracts. One hundred cc. of the original extract were titrated with 0.1 *N* sodium hydroxide, using phenolphthalein as indicator. The end-point was taken as the point at which the alkali produced a pink color, permanent for one minute. In the tables the results are stated as the number of cc. of 0.1 *N* sodium hydroxide required to neutralize the entire extract from a 50 g. sample.

NITROGEN PRECIPITATED BY TANNIN AND SALT—Proteose and peptone nitrogen were determined by the method of Bigelow and Cook.[1] Fifty cc. portions of the extract, after removal of coagulable protein, were treated in a 100 cc. volumetric flask with 15 g. of sodium chloride, and, when the latter was thoroughly dissolved, chilled to ice-box temperature (12° C.), treated with 30 cc. of a 24 per cent solution of tannic acid (cold), made up to volume with cold water, shaken, and allowed to stand at the temperature of the ice-box for 24 hrs., after which the precipitate was filtered off. The solution was kept cold, and the nitrogen in 50 cc. of the filtrate was determined according to the usual Kjeldahl procedure, except that the addition of potassium sulfate was unnecessary because of the large amount of sodium chloride present. Care was taken during the early part of the oxidation that the escaping hydrochloric acid did not cause the material to foam out of the flask. Since tannic acid invariably contains a certain amount of nitrogen, a blank determination must be made with every experiment. The per cent nitrogen in the tannin salt precipitate was obtained by subtracting the per cent of nitrogen in the tannin salt filtrate from the per cent of non-coagulable nitrogen. The results obtained by this method were sometimes erratic but are included in the table as an indication of changes in peptone and proteose nitrogen.

PROTEOSE NITROGEN BY ZINC SULFATE PRECIPITATION—For this determination 50 cc. of the filtrate from the coagulated protein were concentrated to 30 cc. in a 100 cc. beaker and the resultant solution was saturated with zinc sulfate, according to the method of Bömer.[2] When cold, the solution was filtered through a thin asbestos layer in a Gooch crucible and the precipitate washed with a saturated solution of zinc sulfate. The precipitate, together with the asbestos mat, was transferred to a Kjeldahl flask, and the nitrogen determined as usual.

NITROGEN IN PEPTONE BASES, ETC.—The figures under this heading in the tables were obtained by subtracting the sum of the amine and ammonia nitrogen, amino-acid nitrogen, proteose nitrogen, and coagulable nitrogen from the total soluble nitrogen.

AMINO-ACID NITROGEN—This determination was made according to the general method of Sörensen[3] on 50 cc. of the filtrate after removal of coagulable nitrogen in the extract. The presence of ammonia and the amines tends to interfere with the Sörensen titrations for amino acid but the results have comparative value in detecting changes during cold storage.

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[1] *J. Biol. Chem.*, **33** (1918), 486.

[1] *J. Am. Chem. Soc.*, **28** (1906), 1485.

[2] *Z. anal. Chem.*, **34** (1895), 563.

[3] *Biochem. Z.*, **7** (1907), 64.

AMMONIA AND AMINE NITROGEN BY AËRATION—Portions of 150 cc. of the original extract were analyzed for ammonia in the same manner as the fish flesh.

DETERMINATION OF FAT CONSTANTS—The methods employed for the gross extraction of the oil from the flesh and for the determinations of specific gravity, index of refraction, iodine number, saponification number and acid value of the oil are the same as those described by the writers.[1]

In the tables, the average of two or more concordant determinations is given in every case.

OBSERVATIONS AND RESULTS OF CHEMICAL ANALYSES

(1) *Unglazed Eviscerated Weakfish Stored without Wrapping* (*Series 1001*)

APPEARANCE AFTER STORAGE—These weakfish, stored with neither a glaze nor parchment wrapping, were unmarketable at the end of 4 mo. The whole fish were dried and wrinkled in appearance, while the noses and eyes were whitish and dried out.

At the end of 8 mo. this lot of fish was very uninviting in appearance and unmarketable. As they were unfit for food, no further samples were taken after 8 mo. of storage. The whole fish were badly wrinkled, and white. The eyes were also white and sunken. When cooked the flesh seemed tasteless and dry.

GROSS ANALYSIS—The quantitative variations in the composition of certain fish due to season, age, and individual differences are often very great, as shown by previous investigators and confirmed by the present writers,[2] and the differences attributable to the two latter causes must be borne in mind before giving undue emphasis to variations in the gross analysis of cold stored fish in the accompanying tables. The tendency to lose moisture during storage is common to all flesh products. The loss of moisture from these unglazed fish was greater than that from any of the other fish as shown by the chemical analysis. The percentage of fat varied greatly but this is a characteristic of weakfish and was not due to changes in cold storage. The acidity of the aqueous extract showed no definite change.

NITROGENOUS CONSTITUENTS—Any of the minor but significant changes due to bacterial or enzyme action on the nitrogenous constituents of the stored fish would be indicated by the amounts of such constituents, but more especially by their relation to the total nitrogen, commonly called the "distribution of nitrogen." In general, these unglazed weakfish at the end of 8 mo. showed no greater changes in their nitrogen distribution than the glazed eviscerated weakfish (Series 1002) at the same period. Apparently, 8 mo. of storage temperatures did not produce significant alteration in the nitrogenous constituents of the frozen weakfish even without the protection of this glaze. Ammonia and amine nitrogen increased in amount, but only at about the same rate as in the glazed weakfish. The changes in the soluble and coagulable nitrogen were irregular.

CONSTANTS OF FAT EXTRACTED FROM THE FLESH—Since there is known to be considerable variation in the chemical properties of oils from individual fish, depending on their food, the relation to time of spawning, etc., it does not seem wise to consider that any of the changes in the composition of the fat in these fish, as recorded in Table IV, were due primarily to storage except in the case of the acid value.[3] This value at the end of the 8 mo. storage period showed a considerable increase as compared with that of the oil of the fish when first frozen. However, this change in the acid value was of the same magnitude as that of glazed weakfish (Series 1002) at the same period. Although this lot of weakfish did not have the protection of either glaze or wrapping, it showed no greater signs of aging than similar glazed fish; hence, we may conclude that the slight changes in oils of these frozen fish during the 8 mo. of storage are probably not due to their oxidation by oxygen of the air.

(2) *Glazed Eviscerated Weakfish Stored without Wrapping* (*Series 1002*)

APPEARANCE AFTER STORAGE—Up to the end of 13 mo. the fish of this lot looked bright under their glaze and were neither white nor wrinkled, except to a slight extent on the nose. The eyes were bright but slightly sunken. After cooking, the flesh had a normal appearance and flavor.

After 2 yrs. in storage all of these weakfish were unmarketable owing to the whitish and wrinkled appearance, especially of the heads. The eyes were opaque and much sunken, and the gills yellow and dry. Some of the fins were yellowish and dry. When cooked, they were not unpalatable, but tasteless and flat.

GROSS ANALYSIS—There were no noteworthy changes in the amounts of the various constituents during storage, aside from the usual variations found in the composition of fish of the same species even when of nearly uniform size and taken from the same school. Loss of moisture based on percentage of fat-free solids continued to occur until the twelfth month of storage, after which the results do not seem to indicate further loss of moisture. There was no definite increase in the acidity of the aqueous extract of the flesh.

NITROGENOUS CONSTITUENTS—The percentage of ammonia and amine nitrogen made slight but definite increases during storage. However, these increases were not as marked or as uniform as in the case of frozen bluefish (Series 1006). The per cent of total soluble nitrogen increased up to the eighth month, then decreased. The per cent of coagulable nitrogen showed a similar rise and fall. The percentages of amino-acid nitrogen, as determined by the Sörensen titration method, showed a slight tendency to increase in the storage fish.

CONSTANTS OF FAT EXTRACTED FROM THE FLESH—The only fat constant which changed during storage was the acid value, the latter increasing at an irregular rate during the entire storage period of 2 yrs. and 1 mo. As this was interstitial fat, the increase in the acid value was probably due to enzyme action rather than to bacterial or oxidation changes which might affect external fat. From unpublished work, it is known that the flesh of properly frozen fish is practically sterile.

(3) *Unglazed Eviscerated Weakfish Stored with Paper Wrapping* (*Series 1003*)

APPEARANCE AFTER STORAGE—After 8 mo. these wrapped fish appeared somewhat dried out and wrinkled on the heads. The eyes were sunken and dull but not opaque. After cooking, the flesh tasted normal in every way. At the end of 13 mo. the fish were entirely unmarketable, being much wrinkled and white with opaque and deeply sunken eyes. As their condition was so bad, it was not deemed necessary to carry further the studies on these unglazed wrapped fish. When cooked, they tasted flat and stringy, with a slight bitter after-taste.

GROSS ANALYSIS—The most striking fact about the composition of the fish in this lot is that they were badly dried out at the end of 13 mo. storage. Judging by chemical analysis and by appearance, the wrapping around these unglazed fish slightly retarded their desiccation but did not keep them from becoming unmarketable and unfit for food after 13 mo. The ordinary food constituents showed no significant changes.

NITROGENOUS CONSTITUENTS—As usual, there was a gradual increase in the percentage of ammonia and amine nitrogen during storage for 13 mo. However, this increase was no more marked than that found in glazed weakfish stored for about the same period. Like the glazed fish (Series 1002) the total soluble nitrogen and the non-coagulable nitrogen increased to the eighth month, then fell.

CONSTANTS OF FAT EXTRACTED FROM THE FLESH—There was the usual increase in the acid value of the oils from the fish after 13 mo. of storage. The magnitude of this change was about the same in the case of the glazed weakfish (Series 1002) after storage for the same period.

(4) *Glazed Weakfish Stored with Entrails Intact and without Wrapping* (*Series 1004*)

APPEARANCE AFTER STORAGE—After storage for 13 mo., the appearance of these fish was still good, only the slightly sunken condition of the eyes indicating aging. One of the weakfish in this lot had in its stomach 4 small fish about 6 in. long. None of these ingested fish showed any signs of enzyme action on the part of digestive juices or bacteria. However, at the end of storage for 2 yrs., the fish were entirely unmarketable owing to their general wrinkled and whitish appearance and sunken dull white eyes. Upon cooking, the flesh was tasteless and poor in quality, though not inedible.

GROSS ANALYSIS—There were no noteworthy changes in the percentages of the ordinary food constituents during storage.

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[1] *J. Biol. Chem.*, **33** (1918), 487, 493.

[2] *Ibid.*, **33** (1918), 483.

[3] Analyses of a large number of fish have shown that the acid value of the fat varies with the content of fat. In general the lean fish have a higher acid value than the fat fish of the same species. This relationship between the acid value of the fat and the state of nutrition of the fish is being studied further. Consideration has been given to this factor in arriving at conclusions in regard to changes due to storage.

Table I—Gross Flesh Analysis

					Per cent on Moist Basis						Per cent on Dry Basis			
No.	Description of Fish	Storage Period	Weight of Fish Analyzed G.	Edible Portion Per cent	Moisture	Fat-free Solids	Ash	Ether Extract	Total Nitrogen	Ammonia and Amine Nitrogen	Ash	Ether Extract	Total Nitrogen	Ammonia and Amine Nitrogen
	Weakfish													
1002/1	Eviscerated	Fresh	1273	55.1	75.59	19.26	1.18	5.15	3.00	0.016	4.83	21.10	12.29	0.065
1002/2		Fresh	1104	50.0	78.70	19.54	1.24	1.76	2.96	0.018	5.82	8.26	13.89	0.084
1001/1	Eviscerated, not glazed, not wrapped in paper	1 mo.	1585	51.9	75.86	20.77	1.14	3.37	3.06	0.014	4.72	13.96	12.67	0.059
1001/2		2 mo.	1840	50.3	75.98	20.67	1.08	3.35	3.12	0.018	4.50	13.94	12.98	0.073
1001/3		4 mo.	1597	57.6	71.78	20.19	1.12	8.03	3.19	0.016	3.97	28.45	11.34	0.058
1001/4		8 mo.	991	56.5	74.72	22.93	1.31	2.35	3.42	0.024	5.18	9.27	13.53	0.093
1002/1	Eviscerated, glazed, not wrapped in paper	2 mo.	2027	50.6	77.61	20.48	0.96	1.91	2.99	0.017	4.29	8.53	13.35	0.076
1002/2		4 mo.	1655	53.1	76.65	20.88	1.10	2.47	3.13	0.015	4.71	10.59	13.40	0.066
1002/3		8 mo.	1657	45.5	76.92	21.09	1.18	1.99	3.12	0.023	5.11	8.62	13.52	0.101
1002/4		1 yr. 1 mo.	1543	52.8	75.14	22.04	1.16	2.82	3.20	0.020	4.67	11.34	12.87	0.081
1002/5		2 yrs. 1 mo.	2123	51.5	75.16	21.97	1.10	2.87	3.17	0.023	4.42	11.54	12.75	0.091
1003/1	Eviscerated, not glazed, wrapped in paper	4 mo.	1660	51.7	77.12	21.53	1.16	1.35	3.13	0.019	5.07	5.90	13.67	0.083
1003/2		8 mo.	1721	56.3	72.87	20.96	1.16	6.17	3.16	0.021	4.28	22.74	11.64	0.076
1003/3		1 yr. 1 mo.	1505	52.3	75.57	22.03	1.28	2.40	3.30	0.023	5.24	9.82	13.50	0.093
1004/1	Not eviscerated, glazed, not wrapped in paper	4 mo.	1528	47.2	74.49	20.63	1.16	4.88	3.09	0.019	4.55	19.13	12.11	0.075
1004/2		10 mo.	1518	48.9	75.95	20.98	1.14	3.07	3.12	0.030	4.74	12.76	12.97	0.125
1004/3		1 yr. 1 mo.	1858	43.9	75.41	21.40	1.13	3.19	3.18	0.028	4.60	12.97	12.93	0.112
1004/4		2 yrs. 1 mo.	1863	42.8	75.77	20.52	1.13	3.71	3.12	0.032	4.66	15.31	12.88	0.132
	Bluefish													
1006/1	Eviscerated	Fresh	5432	50.0	76.02	22.85	1.34	1.13	3.44	0.019	5.58	4.71	14.34	0.081
1006/2		Fresh	2982	51.4	75.64	22.54	1.32	1.82	3.31	0.024	5.41	7.40	13.58	0.097
1006/1	Eviscerated, glazed, not wrapped in paper	4 mo.	4354	52.3	74.20	22.47	0.99	3.33	3.34	0.016	3.84	12.90	12.94	0.060
1006/2		5 mo.	5030	49.5	73.98	22.83	1.14	3.19	3.41	0.022	4.38	12.26	13.10	0.082
1006/3		8 mo.	4250	48.4	74.32	23.66	1.27	2.02	3.56	0.025	4.95	7.87	13.82	0.097
1006/4		1 yr.	4801	47.7	74.74	23.41	1.22	1.85	3.37	0.029	4.83	7.32	13.34	0.114
1006/5		1 yr. 4 mo.	4210	53.9	74.29	23.90	1.23	1.81	3.37	0.026	4.78	7.04	13.10	0.100
1006/1*a*		1 yr. 4 mo.	3930	51.4	75.67	23.70	1.26	0.63	3.56	0.021	5.18	2.59	14.63	0.067
1006/6		2 yrs. 3½ mo.	3796	51.0	73.78	24.89	1.23	1.33	3.63	0.028	4.69	5.07	13.85	0.107

NITROGENOUS CONSTITUENTS—With the exception of the pronounced tendency of ammonia and amine nitrogen to increase in these uneviscerated weakfish, there were no other changes different from these discussed in the case of the glazed eviscerated weakfish (Series 1002). No other lot of fish exhibited such a tendency to form ammonia and amine nitrogen as did the weakfish stored "in the round." As all the lots of weakfish came from the same school, and had a normal uniform content of nitrogen in this form at the start, it would appear that the presence of the entrails in the fish during storage was concerned in this matter. The importance of this question, however, is such that until further study has been made no definite conclusions should be drawn.

CONSTANTS OF FAT EXTRACTED FROM THE FLESH—Except for the usual increase in the acid value there were no significant changes in the composition of the fat of these fish as revealed by chemical analyses.

(5) *Glazed Eviscerated Bluefish Stored without Wrapping* (*Series 1006*)

APPEARANCE AFTER STORAGE—There were no noticeable changes in the appearance of these bluefish until the end of 16 mo. of freezer storage. When removed at the end of the sixteenth month, the lot showed a certain amount of drying out on the noses of the fish, which were wrinkled and yellowish; the eyes were somewhat sunken, but eyes and skin were fairly bright. Upon cooking, the flesh was palatable and the flavor did not noticeably differ from that of fresh bluefish. These fish were in marketable condition and only a person familiar with the appearance of frozen fish would have classed them as "old stock."

The bluefish which were in storage for 2 yrs. and 3.5 mo. were in unmarketable condition when taken out for analysis. The noses and skin were dried, wrinkled, and yellowish. The gills were dry and brown. Some of the fins were swollen and soft. The eyes were sunken and opaque. The flesh seemed soggy after thawing but there was no odor of decomposition, only a peculiarly strong fishy odor. Upon cooking, the parts of the flesh near the skin were bitter and unpalatable, while the interior portions had a good flavor but were tough. As the fish had been kept glazed during the whole period of storage, there had been no opportunity for molds to attack their surface. From every point of view these fish were unmarketable and hardly fit for food.

GROSS ANALYSIS—There were no variations in the proportions of the gross food constituents of bluefish which could not be explained as being due to a loss of moisture during the periods of storage or to natural variations in the composition of this species of fish. The difference between the average initial per cent of fat-free solids and the per cent of this constituent at the end of the several periods of storage indicates a gradual loss of moisture amounting to about 0.7 per cent at the end of one year and to about 2.2 per cent at the end of 2 yrs. and 3.5 mo., in spite of the protection afforded by the ice glaze. At the close of the latter period the physical appearance of the fish confirmed the analytical findings in this regard. The acidity of the aqueous extracts showed no change.

NITROGENOUS CONSTITUENTS—There is a slight but definite tendency for the percentage of ammonia and amine nitrogen to increase during storage, both as determined on the flesh itself and on its aqueous extract. There was a considerable decrease in the amount of coagulable nitrogen after one year of storage. The proportion of soluble nitrogen showed a less marked decrease. Proteose nitrogen, as determined by zinc sulfate precipitation, was another constituent that decreased perceptibly during storage.

CONSTANTS OF FAT EXTRACTED FROM THE FLESH—The acid value of the oil of the bluefish showed a definite increase during storage and a relatively high value at the end of over 2 yrs. In addition there appeared to be a decrease in the iodine number. This may have been due to a slight oxidation of the oil, a change which probably was wrought by the action of the air on the oil near the surface of the fish after this part of the fish had become somewhat dried out.

DISCUSSION

One of the inevitable effects of cold storage upon frozen fish is loss of moisture. This evaporation of water at temperatures from —5° to 15° F. is indeed slow, and within certain limits decreases in amount with decreasing temperatures. At the beginning of the storage period the proportion of fat-free solids in the freshly frozen weakfish averaged 19.40 per cent. After 8 mo. the fat-free solids (Table I) of the frozen weakfish, which had been stored in the eviscerated condition without a protective coating of ice-glaze or paper, were 22.93 per cent, indicating a decrease of 3.53 in the per cent of moisture. In contrast to this, the fat-free solids of the frozen weakfish, which had been stored for 25 mo. in the eviscerated condition and "sealed" with a thin layer of ice, were 21.97 per cent, corresponding to a decrease of 2.5 in the per cent of moisture. It is plain that the ice-glaze greatly retarded evaporation of water from the flesh. This slight desiccation of the fish is shown, not only by chemical analysis, but by the appearance as well. The unglazed fish stored without wrapping were unmarketable at the end of 4 mo. owing to their dried-out appearance, whereas the glazed fish were in marketable condition even at the end of 13 mo. Loss of

Table II—Composition of the Cold Water Extract of the Flesh

			Per cent on Moist Basis											Per cent on Water-, Ash-, and Fat-free Basis						
							Nitrogen							Nitrogen						
No.	Description of Fish	Storage Period	Solids	Ash	Organic Matter	Acidity of Extract Cc.	Total	Coagulable	In Peptone Bases, etc. (by Difference)	In Tannin-Salt Precipitate	Proteose	Amino Acid	Ammonia and Amine	Total	Coagulable	In Peptone Bases, etc. (by Difference)	In Tannin-Salt Precipitate	Proteose	Amino Acid	Ammonia and Amine
	Weakfish																			
1002/1	Eviscerated	Fresh	7.49	1.04	6.45	15.4	0.858	0.547	0.233	0.040	0.010	0.054	0.014	4.75	3.03	1.29	0.221	0.055	0.298	0.082
1002/2		Fresh	7.28	1.11	6.18	15.0	0.771	0.499	0.228	0.033	0.017	0.054	0.015	4.21	2.45	1.29	0.180	0.092	0.295	0.081
1001/1	Eviscerated, not glazed, not wrapped in paper	1 mo.	5.83	1.07	4.76	15.1	0.906	0.554	...	0.029	...	0.090	0.013	4.62	2.82	..	0.250	...	0.458	0.068
1001/2		2 mo.	6.04	1.08	4.96	17.8	0.821	0.489	0.232	0.031	0.012	0.074	0.014	4.16	2.45	1.16	0.158	0.060	0.377	0.072
1001/3		4 mo.	7.28	1.05	6.23	13.6	0.793	0.482	0.202	0.027	0.020	0.074	0.015	4.15	2.52	1.06	0.144	0.103	0.389	0.077
1001/4		8 mo.	8.88	1.21	7.67	16.4	0.998	0.628	0.266	0.030	0.011	0.076	0.017	4.62	2.90	1.24	0.139	0.052	0.352	0.078
1002/1	Eviscerated, glazed, not wrapped in paper	2 mo.	6.23	0.97	5.26	18.5	0.834	0.494	0.235	0.035	0.010	0.082	0.013	4.27	2.53	1.18	0.179	0.050	0.421	0.086
1002/2		4 mo.	4.10	1.05	3.05	15.1	0.843	0.515	0.220	0.026	0.015	0.078	0.015	4.26	2.60	1.13	0.132	0.075	0.393	0.076
1002/3		8 mo.	4.22	1.14	3.08	16.0	0.949	0.631	0.216	0.045	0.010	0.073	0.019	4.77	3.17	1.09	0.234	0.047	0.365	0.095
1002/4		1 yr. 1 mo.	7.28	0.97	6.31	16.0	0.807	0.493	0.224	0.034	0.013	0.060	0.017	3.86	2.36	1.07	0.163	0.063	0.286	0.080
1002/5		2 yrs. 1 mo.	7.36	0.97	6.39	18.0	0.813	0.456	0.254	0.029	0.008	0.077	0.018	3.88	2.18	1.21	0.139	0.040	0.367	0.085
1003/1	Eviscerated, not glazed, wrapped in paper	4 mo.	4.77	1.07	3.70	16.6	0.866	0.511	0.262	0.039	0.015	0.064	0.014	4.25	2.51	1.29	0.192	0.073	0.312	0.068
1003/2		8 mo.	7.85	1.08	6.73	17.0	0.897	0.546	0.256	0.018	0.011	0.071	0.013	4.53	2.76	1.29	0.191	0.057	0.357	0.066
1003/3		1 yr. 1 mo.	7.56	1.02	6.54	18.6	0.835	0.499	0.235	0.021	0.011	0.075	0.015	4.02	2.40	1.14	0.101	0.052	0.360	0.072
1004/1	Not eviscerated, glazed, not wrapped in paper	4 mo.	4.48	1.07	3.41	16.0	0.855	0.520	0.233	0.024	0.014	0.071	0.017	4.39	2.67	1.20	0.125	0.074	0.363	0.086
1004/2		10 mo.	7.23	1.05	6.18	25.5	0.992	0.658	0.205	0.026	0.021	0.087	0.021	5.00	3.32	1.03	0.131	0.104	0.438	0.104
1004/3		1 yr. 1 mo.	7.72	0.97	6.75	15.6	0.849	0.515	0.221	0.026	0.015	0.073	0.025	4.19	2.05	1.58	0.128	0.073	0.361	0.124
1004/4		2 yrs. 1 mo.	7.67	0.96	6.71	15.5	0.805	0.452	0.228	0.045	0.015	0.084	0.026	4.15	2.38	1.14	0.232	0.077	0.421	0.132
	Bluefish																			
1006/1	Eviscerated	Fresh	7.16	1.24	5.92	35.4	0.933	0.479	0.281	0.045	0.054	0.102	0.017	4.34	2.23	1.31	0.200	0.251	0.474	0.078
1006/2		Fresh	8.50	1.30	7.20	36.0	1.064	0.580	0.310	0.054	0.050	0.107	0.017	5.01	2.73	1.46	0.254	0.233	0.504	0.079
1006/1	Eviscerated, glazed, not wrapped in paper	4 mo.	4.54	1.14	3.40	30.0	0.769	0.421	0.175	0.055	0.044	0.113	0.016	3.58	1.96	0.82	0.254	0.203	0.526	0.074
1006/2		5 mo.	5.65	1.24	4.41	27.1	0.760	0.329	0.266	0.012	0.035	0.112	0.018	3.50	1.52	1.22	0.055	0.162	0.514	0.081
1006/3		8 mo.	5.49	1.17	4.32	28.0	0.818	0.440	0.220	0.056	0.034	0.103	0.021	3.65	1.96	0.99	0.250	0.149	0.459	0.093
1006/4		1 yr.	6.80	1.19	5.61	38.0	0.849	0.311	0.329	0.050	0.044	0.143	0.022	3.82	1.40	1.48	0.227	0.197	0.645	0.097
1006/5		1 yr. 4 mo.	6.27	1.15	5.12	36.1	0.785	0.302	0.319	0.041	0.028	0.112	0.024	3.45	1.33	1.40	0.180	0.124	0.492	0.106
1006/1*a*		1 yr. 4 mo.	6.98	1.18	5.80	31.4	0.863	0.351	0.350	0.071	0.021	0.120	0.021	3.84	1.56	1.46	0.316	0.094	0.636	0.091
1006/6		2 yrs 3½ mo.	7.22	1.23	5.99	37.4	0.863	0.332	0.334	0.058	0.032	0.137	0.028	3.65	1.40	1.42	0.245	0.134	0.579	0.118

moisture is also slightly retarded by wrapping the fish in semi-parchment paper, although it is plain that the paper alone gives insufficient protection from the drying effects of the air. Glazing seals the fish in an almost air-tight manner, and is evidently a necessary precaution to preserve the bright and fresh appearance of fish when removed from storage. It is known that ordinary glazing processes add from 3 to 5 per cent to the weight of the fish, but, on the other hand, during storage both the fish and the glaze lose weight as a result of the evaporation of water.

The rate of evaporation of water from the flesh of the glazed weakfish appeared to decrease markedly after the fish had been in storage for a year (Fat-free Solids, Table I). The losses of moisture from the flesh of all the glazed fish during the first 8 or 10 mo. of storage were small and not such as to produce a material change in the appearance of the fish. Except for an occasional broken or dried fin these fish after thawing resembled closely those often found in markets and sold as fresh fish. This good showing was due to the fact that the fish were frozen in cakes, conforming to the size of the usual commercial pan used for the initial freezing, thus reducing the amount of surface exposed to the air; to the protection afforded by the ice-glaze, which was renewed as required; and to the uniformly low temperature (15° F.) at which the fish were kept. In most commercial fish freezers in this country even better results might be expected, as the average temperature of their storage rooms is 5° or 10° (F.) lower than that of the rooms in which the experimental fish were held.

There is no evidence to show that the proportions of the food constituents of fish, namely, fat, protein, and ash, underwent appreciable changes in cold storage. At first glance it would seem that the variations in the amounts of these constituents in individual fish of the same school are surprisingly great. However, this lack of uniformity in composition is due almost entirely to the variations in the fat content, which is for the most part compensated for by changes in the moisture content. When due allowance is made for this natural variation, the proportions of protein, as represented by nitrogen in the tables, and ash do not change during storage except by amounts which can be accounted for by the slight loss of moisture.

Upon autolysis or bacterial attack the flesh of fish yields both ammonia and amines. In comparative investigations, such as here presented, the sum of the ammonia and amine nitrogen, or nitrogen determined by aëration, may be used as one index of changes in the nitrogenous constituents of fish flesh during storage. It is impossible to say whether such observed changes are due primarily to enzyme action or to the growth of bacteria. In either case, the nitrogen determined by aëration represents end-products which collect and indicate aging processes in fish. During storage there seemed to be a slight tendency for ammonia and amine nitrogen to increase, but this was usually not marked until after one year of storage. Bluefish had a more pronounced tendency to form ammonia and amine nitrogen than most of the lots of weakfish. In the latter, the effects of glazing and wrapping on the production of this form of nitrogen were not apparent. However, the weakfish which were stored with entrails intact exhibited a relatively

TABLE III—NITROGEN DISTRIBUTION CALCULATED IN PER CENT OF TOTAL NITROGEN

				Per cent Nitrogen						
No.	Description of Fish	Storage Period	Total	Soluble	Coagulable	In Peptone Bases, etc. (by Difference)	In Tannin-Salt Precipitate	Proteose	Amino Acid	Ammonia and Amine
	Weakfish									
1002/1	Eviscerated	Fresh	100	28.60	18.26	7.71	1.33	0.33	1.80	0.50
1002/2		Fresh	100	26.13	15.21	8.01	1.12	0.57	1.83	0.51
1001/1	Eviscerated, not glazed, not wrapped in paper	1 mo.	100	29.61	18.07	..	1.60	..	2.93	0.44
1001/2		2 mo.	100	26.25	15.64	7.40	1.00	0.38	2.38	0.45
1001/3		4 mo.	100	24.82	15.07	6.36	0.86	0.61	2.32	0.46
1001/4		8 mo.	100	29.19	18.33	7.81	0.88	0.33	2.23	0.49
1002/1	Eviscerated, glazed, not wrapped in paper	2 mo.	100	28.07	16.63	7.78	1.18	0.32	2.77	0.57
1002/2		4 mo.	100	26.93	16.43	7.06	0.83	0.48	2.48	0.48
1002/3		8 mo.	100	30.44	20.23	6.98	1.49	0.30	2.33	0.60
1002/4		1 yr. 1 mo.	100	25.19	15.40	6.89	1.06	0.40	1.87	0.63
1002/5		2 yrs. 1 mo.	100	25.66	14.37	8.05	0.92	0.26	2.42	0.56
1003/1	Eviscerated, not glazed, wrapped in paper	4 mo.	100	27.67	16.34	8.38	1.26	0.48	2.03	0.44
1003/2		8 mo.	100	28.38	17.29	8.08	0.57	0.35	2.24	0.42
1003/3		1 yr. 1 mo.	100	25.28	13.09	9.16	0.64	0.32	2.26	0.45
1004/1	Not eviscerated, glazed, not wrapped in paper	4 mo.	100	27.66	16.82	7.54	0.79	0.47	2.29	0.54
1004/2		10 mo.	100	31.80	21.12	6.57	0.83	0.66	2.79	0.66
1004/3		1 yr. 1 mo.	100	26.72	13.07	10.10	0.82	0.46	2.30	0.79
1004/4		2 yrs. 1 mo.	100	25.82	14.81	7.09	1.44	0.48	2.62	0.82
	Bluefish									
1006/1	Eviscerated	Fresh	100	27.14	13.94	8.18	1.31	1.57	2.96	0.49
1006/2		Fresh	100	32.13	17.51	9.55	1.63	1.33	3.23	0.51
1006/1	Eviscerated, glazed, not wrapped in paper	4 mo.	100	23.00	12.60	5.24	1.63	1.30	3.38	0.48
1006/2		5 mo.	100	22.26	9.67	7.78	0.35	1.03	3.27	0.51
1006/3		8 mo	100	23.04	12.37	6.25	1.58	0.94	2.89	0.59
1006/4		1 yr.	100	25.16	9.22	9.77	1.49	1.29	4.25	0.63
1006/5		1 yr. 4 mo.	100	23.31	8.98	9.45	1.21	0.84	3.32	0.72
1006/1*a*		1 yr 4 mo.	100	24.21	9.84	9.82	1.99	0.59	3.38	0.58
1006/6		2 yrs $3^1/_2$mo.	100	23.79	9.12	9.26	1.60	0.87	3.77	0.77

strong tendency for this constituent to increase. In fact, the highest percentages of ammonia and amine nitrogen found in any case were in those weakfish frozen "in the round." Since these fish were hard frozen it is difficult to conceive that this increase was due to the slow diffusion of decomposition products into the flesh from the entrails or to the penetration of bacteria from the same source. Whatever the explanation may be, it does not seem impossible that these changes in the flesh are traceable to the presence of the entrails during storage. Further experimentation is necessary before a definite conclusion can be reached.

During storage the bluefish showed a decrease in the amounts of water-soluble and coagulable nitrogen. These constituents increased at first and then decreased in all of the weakfish, except those stored in the eviscerated condition without glazing or wrapping, in which the changes were irregular. The nitrogen in the form of peptone, bases, etc., did not seem to be a variable constituent in the case of any of the fish in storage. The proteose and peptone nitrogen, as precipitated by tannin and salt, did not vary appreciably in amount. Proteose nitrogen, as precipitated by the zinc sulfate method, decreased perceptibly in the bluefish during storage, but not in the weakfish. Bluefish seem to contain, naturally, about three times as much proteose nitrogen as weakfish. Bluefish also contain more amino-acid nitrogen than weakfish, and both species show a slight tendency towards the accumulation of this constituent while in storage.

The interpretation of the meaning of the slight changes in the nitrogenous constituents just described is difficult owing to the small amounts involved, the apparently conflicting tendencies, and to the fact that the role of bacteria and enzymes in such changes is unknown for fish flesh in the hard frozen condition. However, the general conclusion to be drawn from the slight changes observed is that they indicate the beginning of the process of the breaking down of the larger protein molecules into intermediate products, and the simple substances like amino acids, and ammonia. Such changes are typical of the decomposition of proteins by enzymes or bacteria in ripening processes. The flesh of fish, unlike that of beef or poultry, is known to yield considerable amounts of amines when attacked by bacteria or enzymes. The changes occurring were very slight and of such a nature as would warrant the belief that they were brought about by autolysis rather than by bacterial action.

The iodine number of the fat of the fish which were analyzed after 2 yrs. of storage seemed to be somewhat lower than that of fish which had been stored for shorter periods. This was most pronounced in the case of the bluefish and is probably due to the oxidizing action of the air on the fats near the surface of the fish which was more or less dried out at this stage.

The increase in the acid value of the oils from frozen bluefish and weakfish was the most striking effect noticed in the storage investigations. The weakfish contained a large and also more variable amount of fat when compared with bluefish. The latter did not show such large increases in acid value as the weakfish. This change began to be most noticeable after 8 mo. or a year in storage. Up to this time neither glazing nor wrapping the fish to protect them from the air seemed to have any effect on this aging process in the fat. For this reason, during this time it is probably not influenced as much by atmospheric oxidation as by the bacterial or tissue enzymes in the flesh of the fish itself. The action of such enzymes at the low temperature of storage is necessarily slow and the acids produced in the fats of these fish did not impart a "rancid" flavor to the flesh of the fish which had been stored for a year in the glazed condition.

During the first 13 or 16 mo. of storage the changes in the chemical composition of the fish which had been frozen and stored under the best conditions were not reflected in changes in the flavor of the product after cooking. During the longer periods of storage, however, an undesirable change in the flavor of the cooked flesh could be detected. However, it should be noted,

TABLE IV—ANALYSIS OF FAT

No.	Description of Fish	Storage Period	Specific Gravity 25/25° C.	Index of Refraction 30° C.	Iodine No.	Saponification No.	Acid Value
	Weakfish						
1002/1	Eviscerated	Fresh	0.9183	1.4745	142.3	185.8	5.5
1002/2		Fresh	0.9315	1.4749	138.9	182.6	12.4
1001/1	Eviscerated, not glazed, not wrapped in paper	1 mo.	....	....	...	...	..
1001/2		2 mo.	0.9188	1.4709	...	192.6	11.7
1001/3		4 mo.	0.9195	1.4726	132.6	194.8	11.4
1001/4		8 mo	0.9216	1.4727	129.6	187.1	23.4
1002/1	Eviscerated, glazed, not wrapped in paper	2 mo.	0.9240	1.4726	...	191.6	17.9
1002/2		4 mo.	0.9207	1.4743	132.9	194.1	16.2
1002/3		8 mo.	0.9254	1.4724	124.9	187.3	25.3
1002/4		1 yr. 1 mo.	0.9266	1.4725	128.3	188.7	20.2
1002/5		2 yrs. 1 mo.	0.9333	1.4740	136.5	184.1	26.1
1003/1	Eviscerated, not glazed, wrapped in paper	4 mo.	0.9267	1.4740	...	180.5	21.3
1003/2		8 mo.	0.9221	1.4728	136.7	190.9	15.9
1003/3		1 yr. 1 mo.	0.9141	1.4704	133.6	177.9	20.1
1004/1	Not eviscerated, glazed, not wrapped in paper	4 mo.	0.9187	1.4724	124.1	194.2	12.8
1004/2		10 mo.	0.9261	1.4731	140.3	191.0	22.4
1004/3		1 yr. 1 mo.	0.9147	1.4703	128.6	182.3	20.2
1004/4		2 yrs. 1 mo.	0.9214	1.4733	128.8	184.1	25.2
	Bluefish						
1006/1	Eviscerated	Fresh	0.9310	1.4786	126.0	178.9	38.9
1006/2		Fresh	....	1.4745	136.4	172.8	16.3
1006/1	Eviscerated, glazed, not wrapped in paper	4 mo.	....	....	...	...	..
1006/2		5 mo.	0.9325	1.4723	137.9	187.9	21.8
1006/3		8 mo.	0.9148	1.4735	126.5	...	27.4
1006/4		1 yr.	0.9286	1.4745	133.4	188.9	34.1
1006/5		1 yr. 4 mo.	0.9078	1.4694	127.5	172.6	32.0
1006/1*a*		1 yr. 4 mo.	0.9269	1.4745	118.8	176.1	40.4
1006/6		2 yrs. $3^1/_2$ mo.	0.9204	1.4710	118.5	181.3	41.6

in connection with the longer storage periods, that the holding temperature (15° F.) is higher than is ordinarily used commercially.

SUMMARY

Two species of salt water fish. *i. e.*, bluefish, *Pomatomus saltatrix*, and weakfish, *Cynoscion regalis*, were frozen by the commonly used air process, stored in a holding room whose temperature remained near 15° F. and examined chemically and organoleptically at the conclusion of holding periods varying in duration from 1 to 27.5 mo. The bluefish before freezing were eviscerated and were kept "glazed" with an ice covering during storage. The weakfish were divided in four lots, each of which was prepared for storage in a different manner in order to determine the effects of glazing, paper wrapping, and the presence of entrails on the keeping quality of these fish.

I—Bluefish and the weakfish stored in the glazed condition remained palatable and wholesome during storage for 16 and 13 mo., respectively.

II—Weakfish, which had not been glazed or otherwise protected against loss of moisture, dried out so rapidly that at the end of 4 mo. they were considered unmarketable.

III—The loss of moisture in weakfish was checked but slightly by wrapping the fish in semi-parchment paper. Paper wrapping is by no means an adequate substitute for the ice-glaze.

IV—The keeping quality of glazed uneviscerated weakfish in storage up to 13 mo. was practically the same as that of the glazed eviscerated weakfish.

V—Both bluefish and weakfish became unpalatable after 2 yrs. of storage. The desiccation and consequent ruining of the appearance of the fish after long periods of holding were more marked than they would have been if the temperature of the storage rooms had been nearer the average commercial holding temperature.

VI—The following changes in the composition of the flesh of the fish during storage were noted:

(*a*) Water-soluble and coagulable nitrogen decreased in the bluefish, and increased at first, then decreased in all weakfish except those stored in the eviscerated condition without glazing or wrapping. In the latter the changes were irregular.

(*b*) Proteose nitrogen decreased in the bluefish but underwent no distinctive change in the weakfish.

(*c*) Amino-acid nitrogen increased slightly in both bluefish and weakfish.

(*d*) Ammonia and amine nitrogen increased markedly in the glazed uneviscerated weakfish and only slightly in the other fish.

(*e*) The acid value of the extracted fat increased in all samples.

(*f*) The iodine number of the extracted fat decreased in all samples, the change being greatest in the bluefish.

SOLID PHASES OBTAINED BY THE EVAPORATION OF CERTAIN SOIL EXTRACTS[1]

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In recent years a very considerable amount of investigation in the Bureau of Soils has been devoted to the nature and functions of soil solution and to water extracts of soils. The results are published in the various bulletins of the Bureau.[2] For the most part these investigations have concerned themselves with the total material extracted and its relation to plant growth and to the so-called plant food constituents. Similarly in various other publications are found more or less extensive accounts of the relation of water to soil dealing with concentration,[1-8,*] movement,[9,10] methods of extraction and materials extracted by water.[11,15] There can also be found in the literature an enormous amount of material dealing with the mineral composition of sea water, saline lakes and deposits, well and drainage waters, etc. These publications are summarized and references found in Clarke's "Data of Geochemistry."[16]

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[1] Published by permission of the Secretary of Agriculture.

[2] See various publications of the Bureau of Soils, U. S. Department of Agriculture, Washington, D. C.

* Numbers refer to Bibliography, p. 668.

In all these articles there is found almost no reference to the actual character of the materials deposited from soil extracts upon evaporation. The usual forms of expression are the relative quantities of ions or radicals found, or a recalculation of these quantities according to conventional formulas supposed to represent the compounds present. In an ordinary soil extract there are, in addition to the organic material present, many inorganic substances other than the so-called plant foods. It is not to be doubted that these may profoundly affect the properties of the soil solutions, and this is particularly true when it is considered that soil solutions become very concentrated as the soils become air-dried and the aqueous films approach or reach saturation. It therefore seemed of interest to determine the nature of the actual salts crystallizable from soil extracts and to determine if possible the variations in these in different types of soils. Many difficulties are encountered in an investigation of this sort, among them being the large volumes of solution and of soil which must be used to secure a workable amount of deposit. The extract contains not only relatively large amounts of organic matter but also considerable quantities of highly colored, non-crystallizable material which very seriously interfere with the petrographic examination of the deposits. Failure to properly estimate the difficulties in advance has rendered the results reported in the following pages somewhat fragmentary and this communication is to be regarded as a preliminary report upon the subject. A more comprehensive investigation is now under way, but the data at hand are of such character as to render their present publication desirable.

EXPERIMENTAL WORK

PROCEDURE—The general plan of operation, with such modifications as seemed advisable as the work developed, was to prepare extracts of the various soils by agitating large quantities with quantities of water ranging from 3 to 5 parts of water to one of soil. The water extract was filtered through Pasteur-Chamberland filters and a portion of the extract evaporated to dryness. The soil and the dry extract were analyzed by the same methods. The main body of the extract was concentrated on a steam bath in a tin-lined copper kettle until crystallization began to take place. Considerable quantities of amorphous and undeterminable material separated before this point was reached. This was filtered off and subjected to complete analysis. The filtrate was allowed to evaporate spontaneously until a crop of crystals appeared. These were filtered off and examined with a petrographic microscope by the ordinary method.

PRELIMINARY WORK—A certain amount of preliminary work was done upon a sample of Chester silt loam from Oakton, Va. The quantity of soil extracted was about 100 kg. and the ratio of soil to water was one to five. After filtering, a portion of the solution was evaporated to dryness and the extract dried at 105° C. This extract was analyzed and the following table gives the composition as compared with a sample of the original soil.

ANALYSIS OF CHESTER SILT LOAM, OAKTON, VA., AND WATER EXTRACT

Analysis by L. A. Steinkoenig

	SOIL	WATER EXTRACT
Loss on ignition	5.30	57.51
Silica, SiO_2	75.37	4.14
Titanium, TiO_2	1.51	0.02
Iron, Fe_2O_3	3.31	0.46
Alumina, Al_2O_3	-12.08	1.78
Manganese, MnO	0.27	0.11
Lime, CaO	0.30	10.52
Magnesia, MgO	0.35	4.84
Potash, K_2O	1.44	11.36
Soda, Na_2O	0.38	8.71
Phosphoric acid, P_2O_5	0.23	0.13

The greater portion of the extract was evaporated in an open kettle until a separation of solid material began, when it was transferred to a porcelain dish and evaporated under a pressure of 15 mm. As soon as a separation of a few grams of solid material had taken place the evaporation was interrupted and the solid material removed by filtration or decantation. In this manner 13 successive fractions were obtained, the last being a pasty mass of the total remaining material. The examination of the fractions of solid material was very difficult because of the precipitation of amorphous and highly colored inorganic matter as well as of large quantities of organic substances. Nevertheless by petrographic examination, the following crystalline compounds were identified:

Gypsum, $CaSO_4.2H_2O$
Calcite, $CaCO_3$
Thenardite, Na_2SO_4
Sylvite, KCl
Kieserite, $MgSO_4 + H_2O$
Picromerite, $MgSO_4K_2SO_4 + 6H_2O$
Mirabilite, $Na_2SO_4.10H_2O$
Epsomite, $MgSO_4.7H_2O$
Carnallite, $KMgCl_3.6H_2O$
Soda niter, $NaNO_3$
Halite, NaCl

In view of these interesting results it seemed desirable to pursue the investigation by a comparison of the salts deposited from the water extract of an alkali soil with those deposited from extracts from soils of humid areas.

EXAMINATION OF SAMPLES OF SOIL EXTRACTS—A sample of Yolo clay, secured from near Los Baños, Cal., was subjected to detailed examination. The sample was an alkali crust together with about 6 in. of underlying soil. This soil is described[17] as follows: "The type is a chocolate-brown clay 6 ft. or more in depth—wheat and barley are the principal crops grown. Alfalfa is successfully grown on this type." This soil was selected because, as an alkali soil, the soluble salt content is relatively high.

The solution was prepared by treating 448 lbs. of the air-dry soil with water using 16 lbs. of soil for each extraction. After extraction the solution was filtered and evaporated in a steam-jacketed kettle. The total amount of solution used was 985.6 liters with a soluble salt content of about 2 g. per liter. After evaporation to about one-tenth of its volume the solution was filtered and returned to the kettle for further concentration. The residue was found to contain considerable quantities of carbonate but no estimation of its quantity or definite composition was made. The solution, which had become of an amber color, was slowly concentrated until a sample on cooling showed a deposition of crystals.

The whole of the solution, now about 12 liters in volume, was placed in a porcelain-lined pan and allowed

TABLE I—WHITE ALKALI SOIL

Yolo clay loam 0–4 in. deep from near Los Baños, California. 448 lbs. of air-dry soil—442 lbs. of dry soil—were treated with 985.6 liters of water equivalent to 440 per cent of moisture calculated on the weight of soil used. On evaporation calcites, gypsum, amorphous mineral and organic matter separated out down to a volume of 13,260 cc., when the following minerals separated out in crystalline form

Microscopical work by W. H. Fry

Crop of Crystals	Sp. Gr. of Solution	Temperature ° C.	Volume of Solution. Cc.	Solution on Basis of Original Soil Per cent	Mirabilite, $Na_2SO_4.10H_2O$	Thenardite, Na_2SO_4	Halite, NaCl	Thermonatrite, $Na_2CO_3.H_2O$	Hanksite, $9Na_2SO_4.2Na_2CO_3.KCl$	Epsomite, $MgSO_4.7H_2O$	Picromerite, $MgSO_4.K_2SO_4.6H_2O$	Leonite, $MgSO_4.K_2SO_4.4H_2O$	Aphthitalite, $(KNa)_2SO_4$	Vanthoffite, $3Na_2SO_4.MgSO_4$	Blodite, $MgSO_4.Na_2SO_4.4H_2O$	Loweite, $MgSO_4.Na_2SO_4.2.5H_2O$	Langbeinite, $K_2SO_4.2MgSO_4$	Tri-sodium Phosphate, Na_3PO_4	Kainite, $MgSO_4.KCl.3H_2O$	Soda Niter, $NaNO_3$	Sodium Carbonate, Na_2CO_3	Carnallite, $KMgCl_3.6H_2O$
0	1.103	23	34,084	17.0[1]	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
1	1.247	25	13,260 4.400	6.6 2.2	x	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
2	1.315	24	3,700	1.8	..	x	x	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
3	1.318	23.5	3,353	1.6	..	x	x	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
4	1.304	21.5	2,660	1.3[2]	..	x	x	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
5	1.301	23	2,312	1.2	..	x	x	x	..	..	..	..	..	..	..	..	..	..	..	..	..	..
6	1.288	21	1,920	0.9	..	x	x	x	..	..	..	..	..	..	..	..	..	..	..	..	..	..
7	1.287	23	1,607	0.8	..	x	x	x	..	..	..	..	..	..	..	..	..	..	..	..	..	..
8	1.273	24	1,246	0.6	..	x	x	x	..	..	..	..	..	..	..	..	..	..	..	..	..	..
9	1.294	22	852	0.4	..	x	x	x	x	x	..	..	..	..	..	..	..	..	..	..	..	..
10	1.323	23	447	0.2	..	x	x	x	x	x	x	..	..	..	..	..	..	..	..	..	..	..
11	1.330	21	255	0.1	..	x	x	x	x	x	x	x	x	x	..	..	..	..	..	..	..	..
12	1.375	25	90	0.04	..	x	x	x	x	x	x	x	x	x	x	x	..	..	..	..	..	..
13	1.404	25	42	0.02	..	x	x	x	x	x	x	x	x	x	x	x	x	x	..	..	..	..
14	...	..	24	0.01	..	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x

[1] Optimum water content. [2] Air-dry condition in laboratory.

to cool over night. A crop of well-formed and quite pure crystals of hydrated sodium sulfate separated out, together with a considerable quantity of a gray sediment. The sediment, about 5 g., washed free from soluble sulfates was analyzed and showed the following composition:

Analysis by M. S. Anderson

	Per cent
Loss on ignition (including CO_2)	37.75
Silica, SiO_2	13.05
Iron oxide, Fe_2O_3	Trace
Alumina, Al_2O_3	2.03
Titanium oxide, TiO_2	None
Lime (CaO)	35.30
Magnesia, MgO	9.38
Potash, K_2O	None
Soda, Na_2O	1.78
Carbon dioxide, CO_2	26.80

The evaporation was now allowed to continue, at room temperature, in porcelain-lined dishes. No salt other than hydrated sodium sulfate separated until a concentration of 5,400 cc. was reached and from this point only traces of any solid phase separated until the concentration had reached a volume of 4,400 cc. The whole deposit to this point is described as Crop 1 in Table I.

A second crop of crystals was recovered when a volume of 3,700 cc. was reached. The specific gravity of the mother liquor was also determined. The evaporation was continued at room temperature until, in all, 14 fractions of crystals were obtained. These were examined petrographically and the compounds identified as indicated in Table I.

In Column 5 are given the percentages of the water in each fraction from which crystals were obtained, calculated on the basis of the original soil. It will be noted that no salts crystallized at a moisture content corresponding to the optimum for the soil and that no salts other than sodium sulfate and sodium chloride assumed the solid phase until the concentration became greater than that corresponding to air-dry soil. The residual liquid from Fraction 14 was a thick brown, pasty mass of such character that further petrographic examination was impracticable.

After the work with the extract from 448 lbs. of soil was completed, a 16-lb. sample of the same soil was extracted with water and the extract evaporated to determine the point at which the sodium sulfate began to crystallize. This was found to be at a concentration of 6.6 per cent of the original soil weight. The total solid separated out at this point amounted to 0.02898 g. Its composition was as follows:

Analysis by W. O. Robinson

	Per cent
Silica, SiO_2	13.37
Alumina, Al_2O_3	5.53
Iron oxide, Fe_2O_3	0.58
Calcium carbonate, $CaCO_3$ (calculated)	32.62
Magnesium oxide, MgO	2.45
Potassium oxide, K_2O	0.34
Sodium oxide, Na_2O	15.50
Sulfur trioxide, SO_3	12.70
Phosphorus pentoxide, P_2O_5	Trace
Ignition loss	16.91

The solution from which the solid was removed had a volume of 1,234 cc. with a specific gravity of 1.112 at 28° C. Its composition was found to be

Analysis by W. O. Robinson

	Grams per Liter
Silica, SiO_2	0.34
Alumina, Al_2O_3	Trace
Ferric oxide, Fe_2O_3	Trace
Lime, CaO	0.25
Magnesium oxide, MgO	0.14
Potassium oxide, K_2O	0.48
Sodium oxide, Na_2O	74.49
Phosphorus pentoxide, P_2O_5	0.019
Chlorine	2.34
Sulfur trioxide, SO_3	56.99
Carbon dioxide, CO_2	1.37

HUMID SOILS—In order to contrast the alkali soil extract with a humid soil a sample of sassafras silt loam[17] was collected in the grounds of the Smithsonian Institution in Washington, D. C.

About 400 lbs. of this soil were extracted and 1,250 liters of solution prepared, filtered through Pasteur-Chamberland filters, and evaporated in the steam kettle. The solid material which separated out when the volume was reduced to 33 liters was collected and analyzed. Evaporation was continued to a volume of 1.56 liters and the solid material again collected and analyzed.

The volume of the solution remaining when the more soluble salts began to crystallize was so small that it was not practicable to determine the volume and specific gravity of each successive fraction from which crystal crops were examined.

Analysis by W. O. Robinson

	RESIDUE AT OPTIMUM WATER CONTENT VOLUME 33 L. Per cent	RESIDUE AT AIR-DRY WATER CONTENT VOLUME 1.56 L. Per cent
Loss on ignition	25.13	8.73
Silica, SiO_2	27.91	2.95
Alumina, Al_2O_3	16.84	2.06
Iron oxide, Fe_2O_3	5.41	1.48
Manganese oxide, MnO	0.43	0.06
Copper oxide, CuO[1]	5.08	Trace
Calcium oxide, CaO	8.80	33.62
Magnesium oxide, MgO	2.28	0.48
Potassium oxide, K_2O	0.66	0.68
Sodium oxide, Na_2O	0.54	1.34
Sulfur trioxide, SO_3	3.91	45.15
Phosphorus pentoxide, P_2O_5	0.23	0.05

[1] From steam kettle.

The results of the petrographic examination of the crystal crops are given in Table II, Column 8. The last fractions contained such relatively large quantities of organic matter that petrographic examination was impossible. As a means of getting this material into workable condition it was dried and charred at as low a temperature as possible and the organic material thus destroyed or rendered insoluble. The residue was dissolved in a small amount of warm water and filtered. The filtrate was allowed to evaporate and the fractions of crystallized material examined. In similar manner Crowley silt loam subsoil from Crowley, La., was examined,[17] and also a sample of Stockton clay adobe from Stockton, Cal.[17] One hundred pounds of each soil were used and 375 liters of each solution prepared. The results of these examinations are shown in Table II, Columns 9 and 10.

TABLE II—SALTS FOUND IN SALINE DEPOSITS AND OBTAINED FROM WATER EXTRACTS OF SOILS

					Analysis by W. H. Fry					
SALTS FOUND	(1) Stassfurt Deposits	(2) Sea Water	(3) Great Basin Region	(4) Searles Marsh	(5) White Alkali Soil	(6) Chester Silt Loam	(7) Various Alkali Crusts	(8) Smithsonian Soil	(9) Stockton Clay Loam	(10) Crowley Silt Loam
SINGLE SALTS										
Chlorides										
Sylvite—KCl	x	x	..	..	..	x	x	x	..	..
Halite—$NaCl$	x	x	x	x	x	x	x	x	x	x
Bischofite—$MgCl_2.6H_2O$	x	x	..	..	..	..	..	..	..	..
Sulfates										
Gypsum—$CaSO_4.2H_2O$	x	x	x	x	x	x	x	x	..	x
Anhydrite—$CaSO_4$	x	..	x	x	..	..	..	..	..	..
Celestite—$SrSO_4$	x	..	x	x	..	..	..	..	..	..
Epsomite—$MgSO_4.7H_2O$	x	x	..	..	x	x	..	..	..	..
Kieserite—$MgSO_4.H_2O$	x	x	..	..	..	x	..	..	..	..
Thenardite—Na_2SO_4	..	x	x	x	x	x	x	x	x	x
Mirabilite—$Na_2SO_4.10H_2O$	..	..	x	..	x	x	x	x	..	..
$MgSO_4.6H_2O$	..	x	..	..	..	..	..	..	..	..
Nitrates										
Soda niter—$NaNO_3$	..	..	x	x	x	x	x	..	..	..
Niter—KNO_3	..	..	x	..	..	..	..	..	..	..
Nitrocalcite—$Ca(NO_3)_2.nH_2O$	..	..	x	..	..	..	..	..	..	..
Nitromagnesite—$Mg(NO_3)_2.nH_2O$	..	..	x	..	..	..	..	..	..	..
Carbonates										
Calcite—$CaCO_3$	x	x	x	x	x	x	x	x	x	x
Aragonite—$CaCO_3$	..	..	..	..	..	..	..	..	..	x
Magnesite—$MgCO_3$	..	..	..	..	x	..	..	..	..	x
Thermonatrite—$Na_2CO_3.H_2O$	..	..	x	..	x	..	..	..	..	..
Natron—$Na_2CO_3.10H_2O$	..	..	x	x	..	..	..	..	..	..
Sodium carbonate—Na_2CO_3	..	..	..	..	x	..	..	..	x	x
Phosphates										
Tri-sodium phosphate—Na_3PO_4	..	..	..	..	x	..	..	..	..	..
DOUBLE SALTS										
Chlorides										
Carnallite—$KCl.MgCl_2.6H_2O$	x	x	..	..	x	x	x	x	..	..
Douglasite—$2KCl.FeCl_2.2H_2O$	x	..	..	..	..	..	..	..	..	..
Tachydrite—$CaCl_2.2MgCl_2.12H_2O$	x	..	..	..	..	..	..	..	..	..
Sulfates										
Aphthitalite—$(KNa)_2SO_4$	x	x	..	..	x	..	x	x	..	..
Picromerite—$K_2SO_4.MgSO_4.6H_2O$	x	x	..	..	x	x	x	x	x	x
Leonite—$K_2SO_4.MgSO_4.4H_2O$	x	x	..	..	x	..	..	x	x	..
Langbeinite—$K_2SO_4.2MgSO_4$	x	..	..	..	x	..	..	..	..	..
Blodite—$Na_2SO_4.MgSO_4.4H_2O$	x	x	..	..	x	..	..	x	x	x
Loweite—$2Na_2SO_4.2MgSO_4.5H_2O$	x	..	..	..	x	..	..	x	..	x
Vanthoffite—$3Na_2SO_4.MgSO_4$	x	..	..	..	x	..	..	x	..	..
Glauberite—$Na_2SO_4.CaSO_4$	x	..	x	x	..	..	..	..	..	..
Kalinite—$K_2SO_4.Al_2(SO_4)_3.24H_2O$	..	..	x	..	..	..	..	..	..	..
Sulfates and Chlorides										
Kainite—$KCl.MgSO_4.3H_2O$	x	x	..	..	x	..	..	..	..	..
Sulfohalite—$3Na_2SO_4.2NaCl$	..	..	x	x	..	..	..	..	..	..
Carbonates										
Trona—$Na_2CO_3.NaHCO_3.2H_2O$	..	..	x	x	..	..	x	..	..	..
Gaylussite—$CaCO_3.Na_2CO_3.5H_2O$	..	..	x	x	..	..	x	..	..	..
Dolomite—$MgCa(CO_3)_2$	..	..	x	x	..	..	..	..	..	..
Pirssonite—$Na_2Ca(CO_3)_2.2H_2O$	..	..	x	x	..	..	..	..	..	..
Silicates										
Natrolite—$Na_2Al_2Si_3O_{10}.2H_2O$	..	..	..	..	..	..	..	..	..	..
TRIPLE SALTS										
Sulfates										
Polyhalite—$K_2SO_4.2CaSO_4.MgSO_4.2H_2O$	x	..	..	..	..	..	..	..	..	..
Krugite—$K_2SO_4.4CaSO_4.MgSO_4.2H_2O$	x	..	..	..	..	..	..	..	..	..
Chlorides and Aluminates										
Koenenite—$2MgCl_2.3MgO.Al_2O_3.6H_2O$ (or $8H_2O$?)	x	..	..	..	..	..	..	..	..	..
Sulfates, Carbonates and Chlorides										
Hanksite—$9Na_2SO_4.2NaCO_3.KCl$	..	..	x	x	x	..	x	..	x	..
Carbonates and Chlorides										
Northupite—$MgCO_3.Na_2CO_3.NaCl$	..	..	x	x	..	..	x	..	..	..
Carbonates and Sulfates										
Tychite—$2MgCO_3.2Na_2CO_3.Na_2SO_4$	..	..	x	x	..	..	..	..	..	..
BORATES										
Boracite—$Mg_7Cl_2B_{16}O_{30}$	x	..	x	..	..	..	..	..	..	..
Pinnoite—$MgB_2O_4.3H_2O$	x	..	..	..	..	..	..	..	..	..
Hydroboracite—$CaMgB_6O_{11}.6H_2O$	x	..	..	..	..	..	..	..	..	..
Heintzite-hydrous borate of Mg and K, formula doubtful	x	..	..	..	..	..	..	..	..	..
Ascharite—$3Mg_2B_2O_5.2H_2O$	x	..	..	..	..	..	..	..	..	..
Sulfoborite—$2MgSO_4.4MgHBO_3.7H_2O$ or $3MgSO_4.2Mg_3B_4O_9.12H_2O$	x	..	..	..	..	..	..	..	..	..
Borax—$Na_2B_4O_7.10H_2O$	..	..	x	x	..	..	..	..	..	..
Colemanite—$Ca_2B_6O_{11}.5H_2O$	..	..	x	x	..	..	..	..	..	..
Ulexite—$NaCaB_5O_9.8H_2O$	..	..	x	..	..	..	..	..	..	..
Howlite—$H_5Ca_2B_5SiO_{14}$	..	..	x	..	..	..	..	..	..	..
Neocolemanite—$Ca_2B_6O_{11}.5H_2O$	..	..	x	..	..	..	..	..	..	..

The Crowley silt loam extract had the composition as shown by the following analysis:

ANALYSIS OF CROWLEY SILT LOAM EXTRACT

Analysis by W. O. Robinson

	PARTS PER MILLION OF SOLUTION	PARTS PER MILLION OF SOIL
Total solids	103.8	856.0
Silica, SiO_2	17.5	143.0
Alumina, Al_2O_3	Trace	Trace
Iron oxide, Fe_2O_3	Trace	Trace
Lime, CaO	20.4	168.0
Magnesia, MgO	1.9	9.7
Potassium oxide, K_2O	0.5	4.1
Sodium oxide, Na_2O	10.1	83.3
Sulfur trioxide, SO_3	3.7	30.5
Chlorine, Cl	1.8	14.9

ALKALI SOIL CRUSTS—Since complex salts were identified at solution concentrations corresponding to a moisture content a little below that of the air-dry condition of the alkali soil it seemed probable that in soils containing a large soluble mineral content the same minerals should be present in air-dry soils in the solid phase. To determine if this were true 14 alkali soil crusts from Ventura County, Cal., and from Arizona were selected and examined by means of the petrographic microscope. The soils were examined without other treatment than pulverization and no attempt was made to secure especially dry samples. The highest number of soluble salts identified in any one soil was 8 and the total list of different minerals is found in Table II, Column 7.

Water extracts of these soils were made, the extracts analyzed and the analyses calculated to the hypothetical combinations according to the usual method. Table III contains the results, together with the minerals found in the air-dry soils.

TABLE III

PERCENTAGE OF SALTS FOUND IN WATER EXTRACT CALCULATED TO HYPOTHETICAL COMBINATIONS — *Analysis by J. C. Ripperton*

MINERALS ACTUALLY OBSERVED BY PETROGRAPHIC METHOD IN THE SAME SOIL OR CRUST — *Analysis by W. H. Fry*

No.	$CaCl_2$	$CaSO_4$	$MgSO_4$	K_2SO_4	Na_2SO_4	NaCl	Na_2CO_3	$NaHCO_3$	$NaNO_3$	$Na_2SO_4.10H_2O$	Na_2SO_4	$Na_2CO_3.NaHCO_3.2H_2O$	KCl	$CaSO_4.2H_2O$	NaCl	$CaCO_3.Na_2CO_3.5H_2O$	$CaCO_3$	$MgSO_4.K_2SO_4.6H_2O$	$MgCO_3.Na_2CO_3.NaCl$	$Na.NO_3$	$Na_2(SO_4)_4.Na_2CO_3$	$KMgCl_3.6H_2O$	$(KNa)_2SO_4$
1	...	22.74	5.75	1.69	...	51.33	...	3.33	..	..	x	..	..	x	x	..	x	..	..	..	..	..	..
2	...	11.22	19.65	3.55	47.66	14.22	1.59	1.89	0.22	x	x	x	x	x	x	x	x	..	..	..	..	..	..
3	...	1.89	1.50	5.02	16.69	51.45	17.84	4.46	1.05	x	..	..	x	x	x	x	x	..	..	..	..	..	..
4	...	7.00	13.30	8.18	59.70	9.79	1.10	0.85	..	x	x	..	..	x	x	..	x	..	..	..	..	..	..
5	...	18.18	11.15	9.08	28.09	33.78	2.14	1.67	..	x	..	..	..	x	x	..	x	..	..	..	..	..	..
6	...	2.75	0.75	12.31	51.80	20.82	4.47	7.04	..	..	x	..	x	x	x	..	x	..	..	..	..	..	..
			$MgCl_2$	KCl																			
7	8.60	10.29	15.56	15.52	...	49.69	...	..	..	..	..	..	x	x	x	..	x	..	..	..	..	..	..
8	...	7.68	6.40	4.37	2.44	77.12	0.42	0.69	0.99	..	..	..	..	x	x	..	x	..	..	..	..	..	..
9	...	4.59	20.55	3.55	60.09	9.24	...	1.19	0.45	x	..	..	x	..	x	..	x	x	..	..	x	x	..
10	...	3.74	28.40	2.19	51.98	12.01	...	1.41	..	x	..	..	x	x	x	..	x	x	..	..	..	..	..
11	...	2.95	6.95	7.56	17.73	27.47	27.19	9.84	..	..	..	..	x	x	x	..	x	..	x	..	x	x	x
12	...	0.24	1.60	1.87	10.70	64.69	14.97	3.06	2.22	..	x	..	..	x	x	x	x	..	x	..	x	..	..
			$MgCl_2$	KCl																			
13	37.58	6.46	8.32	14.08	...	24.98	5.04	3.40	..	..	..	..	..	x	x	..	..	..	..	x	..	..	..
14	...	5.34	2.40	8.96	53.61	12.18	9.67	6.85	0.90	x	x	..	..	x	x	..	x	..	..	..	..	..	..

DISCUSSION OF RESULTS

The existence of complex salts in the crystalline material deposited from the extracts of both alkali and humid soils renders interesting a comparison between these and the natural deposits of saline material and in Table II is given a summarization of the minerals found in Stassfurt deposits[16, 18], the Great Basin region,[19] Searles marsh,[16] and obtained from the evaporation of sea water.[4]

An inspection of the tables reveals the fact that halite, NaCl, and calcite, $CaCO_3$, are the only minerals uniformly present, while gypsum, $CaSO_4.2H_2O$, and thenardite, Na_2SO_4, are next in order of frequency. One of the more notable facts is the occurrence of the more soluble carbonates in the soil extracts and their absence from the deposits from sea water and from the Stassfurt deposits. It is of course not to be expected that the extract from any single soil would deposit the whole range of salts obtained from sea water or in the natural deposits from it since the saline deposits represent the soil extract from the entire globe. It is indeed remarkable that so great a similarity exists. The most notable difference between the soils and soil products is the entire absence of the borates in the latter. This would not be the case, of course, were soils containing borates subjected to examination. The Stassfurt deposits are marked by the absence of thenardite, Na_2SO_4, while carrying large amounts of sulfates in the form of more complex salts. Both the chemical and petrographic analyses indicate that the sulfates, chloride, and carbonates of sodium form by far the greater portion of the soluble material of the soil extract. Hanksite, $9Na_2SO_4.2Na_2CO_3.KCl$, is probably next in abundance, though even this is in very small quantity. The remaining substances identified occur only as traces in the material examined. Although chemical analysis shows the presence of phosphoric acid and of nitrates, it gives no indication of the complexity of the compounds which separate out. It is probable that these salts are present in such small amounts that they may never be present in the solid phase under ordinary soil conditions. As will be seen from Table I, none of the soluble salts crystallize at a concentration corresponding to the optimum moisture content for the alkali soil, and until a concentration corresponding to the air-dry state is reached only sodium sulfate and chloride separate out. It is even more certainly true that in the humid soils the more soluble salts are constantly in solution in the soil moisture film.

It is to be noted with respect to the order of crystallization indicated in Table I for the Yolo clay extract that this order may be expected to vary with different soil extracts and with the temperature at which crystallization takes place. Van't Hoff[21] has given the order of crystallization of minerals from a system containing sodium, potassium, magnesium, sulfate and, chloride in certain proportions as shown in Table IV.

TABLE IV

	HALITE	KIESERITE	KAINITE	CARNALLITE	BISCHOFITE
1.........	95.4	..	..	..	..
2.........	4.42	1.05	2.02	..	..
3.........	0.03	0.35	..	0.1	..
4.........	0.15	0.38	..	0.08	7.62
	100.	1.78	2.02	0.18	7.62
	NaCl	3.8 $MgSO_4$	2.2 KCl	7.8 $MgCl_2$	

In this system halite separates first and continues to come down throughout the process, and the other salts as indicated above, the temperature of the system being maintained at 25° C. The soil solution system is much more complex than this, not only in respect to composition but also in the condition of crystallization. It is not therefore to be expected that the order of crystallization or even the composition of the salts would be just the same as that given in van't Hoff's summarization.[20]

The following geological profile of the Stassfurt deposits arranged in the order of the occurrence of the salts, from the bottom of the deposits upward, has been compiled from the data given by Clarke,[20] and serves as a convenient means of comparison with the results shown in Table I.

- Limestone
- Anhydrite
- Gypsum
- Halite
  - Glauberite
  - Langbeinite
- Polyhalite
- Kieserite
- Carnallite
  - Sylvite
  - Douglasite
  - Tachhydrite
  - Bischofite
- Kainite
  - Blodite
  - Loweite
  - Picromerite
  - Leonite
  - Aphthitalite
  - Vanthoffite
- Epsomite

The marked similarities which are observed are that halite having once begun to crystallize continues to do so during the entire process of evaporation. In the Stassfurt deposits we find a kainite group consisting of a mixture of kainite, blodite, loweite, picromerite, leonite, aphthitalite, and vanthoffite. This entire group is present, and in a comparatively narrow and contiguous range of evaporation in the white alkali extract. In these two respects at least the evaporation products from the white alkali extract very closely resemble the Stassfurt deposits.

All the results given in Tables I to IV indicate that complex salts separate out from soil solutions when evaporation takes place to a sufficient extent and in Table IV data are given which indicate that the conventional method of expression of the analytical data of solution is not only improper by reason of the extensive ionization which takes place in dilute solutions, but is also not justifiable, at least in concentrated solutions, because of the formation of complex salts not represented by the conventional methods of calculation. This observation is not so important, probably, as the following.

There is an accumulating mass of data which indicates that the condition of salts in solution is more complex than we are ordinarily accustomed to consider it, not only by reason of the formation of hydrates but also because of the formation of complex salts and ions, some of which are markedly different in properties from their components. It is not therefore without significance that as soil solutions become more concentrated the tendency toward the formation of complex ions increases and, with saturation, the deposition of complex salts takes place. These therefore may be, and probably are, present in soil moisture as the soil approaches the air-dry condition. The complex salts may very reasonably be assumed to play a role in the fertility of soils. What this role may be, whether beneficial or injurious to plant growth, is not apparent, but that it is of no consequence is not to be assumed. It is also possible that this question may be related to the much vexed one of the part played by fertilizers in soils.

It is to be regretted that this investigation was limited by its conditions in such a way as not to include a study of the organic constituents of the extract and a more detailed examination of the salts present in quantities less in amount or greater in solubility than those identified.

SUMMARY

(1) The salts deposited on the evaporation of the water extract of soils are much more complicated in character than is indicated by a simple statement of the ions existing in solution.

(2) There is a marked general similarity between the salts obtained on the evaporation of water extracts of soils and those obtained by both natural and artificial evaporation of sea water. No soil can be expected to furnish all the salts occurring in natural deposits of saline material because these represent crystallization from a composite soil extract.

(3) Since complex salts begin to separate from a water extract at a point not far from the concentration of an air-dry soil, it follows that the roots of growing plants may be in contact with solutions of these salts. Stated obversely, it is probable that the complex salts obtained from soil extracts may be present in the soils only in solution in soil moisture and never in the solid phase.

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DETERMINATION OF NITRATE NITROGEN IN NITRATES AND FERTILIZERS[1]

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The determination of the nitrate value in nitrate of soda and potash is an important one. Oftentimes a sample represents several thousand tons, and at the present price of these materials it is obvious that wide discrepancies lead to controversies. There have been many methods proposed for this determination, but the majority of them have only a historic interest. Descriptions of these earlier methods, which are scarcely heard of recently, may be found in the literature.[2]

The methods which have been in more or less use recently may be referred to briefly as follows:

I—CONVERSION TO NITRIC OXIDE:

(1) Nitrometer methods[3,4]

(2) Schloesing[3] and Schloesing-Wagner[5] methods

II—DETERMINATION AS AMMONIA:

(1) Reduction in alkaline solutions

  (*a*) Reduction with aluminum[3]

  (*b*) Reduction with zinc dust and iron powder[3,6]

  (*c*) Reduction with Devarda alloy[4]

(2) Reduction in acid solution

  (*a*) Reduction with reduced iron powder[2,6]

  (*b*) Reduction with reduced iron powder and zinc[3]

(3) Phenol-sulfonic acid method (Kjeldahl[2,3,4,5,6]-Gunning)

III—WEST COAST OR REFRACTION METHOD: Determining method water-insoluble matter, chlorine and sulfur trioxide, and calculating as the chloride and sulfate of soda. The difference between the sum of these four results and 100 is called sodium nitrate.

Of the above, the nitrometer methods, or some of those under II, have been in quite general use. Unfortunately the West Coast, or Refraction, method has been very much used, being especially prescribed in contracts governing the imported Chilean nitrate. Doubtless this method would be very accurate if the four impurities named were the only ones found in commercial nitrate, but other impurities also are sometimes present, such as KNO_3, Na_2CO_3, $NaClO_3$, $NaClO_4$, Fe_2O_3, Al_2O_3, CaO and MgO.[1] It is obvious, therefore, that the method favors only the seller, the buyer paying for all ingredients other than the four above named as sodium nitrate.

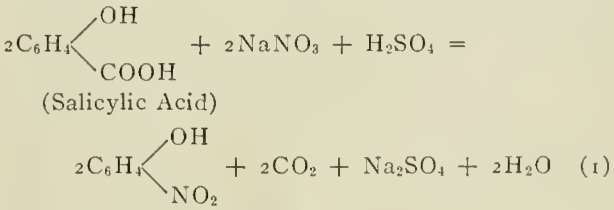
Probably the methods which are in most general use at present are the Nitrometer, Devarda, and Modified Kjeldahl-Gunning. In the fertilizer laboratories either the Modified Kjeldahl or Modified Gunning, or the Modified Kjeldahl-Gunning methods fit most conveniently into the routine. Mr. W. S. Allen[2] described a modification of the Devarda method by which correct results may be obtained. He also reported the analysis of 69 samples by this method and by the West Coast method, and showed that for all of these samples the latter method gave higher results as follows:

Samples	$NaNO_3$ Agreement within per cent
5	0.1
11	0.3
19	0.5
32	0.8
35	1.0
54	1.5
63	2.0
67	2.5
69	3.0

He gives the complete analysis of several samples, showing that when proper allowance for all impurities was made, results by both methods agreed closely. It will be noted that for six of the above samples the buyer would lose from $1.00 to $2.00 per ton by the West Coast result.

MODIFIED KJELDAHL-GUNNING METHOD

The Modified Kjeldahl-Gunning method will be considered here, and when correctly applied will yield extremely accurate results. The method is based upon the following reactions:



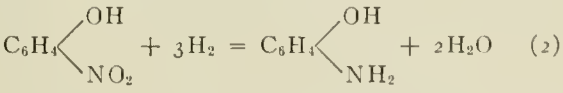
$$2C_6H_4\Big\langle\begin{matrix}OH\\COOH\end{matrix} + 2NaNO_3 + H_2SO_4 =$$

(Salicylic Acid)

$$2C_6H_4\Big\langle\begin{matrix}OH\\NO_2\end{matrix} + 2CO_2 + Na_2SO_4 + 2H_2O \quad (1)$$

(Nitrophenol)

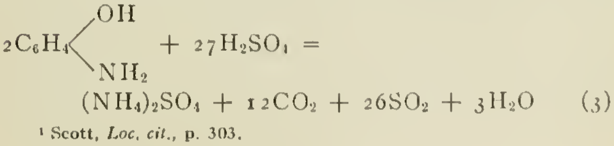
This nitrophenol is next reduced to aminophenol. Just what this reaction is when using "hypo" is not known, since there are present SO_2, H_2S, and free sulfur. The reaction with zinc where hydrogen is liberated is probably as follows:



$$C_6H_4\Big\langle\begin{matrix}OH\\NO_2\end{matrix} + 3H_2 = C_6H_4\Big\langle\begin{matrix}OH\\NH_2\end{matrix} + 2H_2O \quad (2)$$

(Aminophenol)

And finally by continued digestion with sulfuric acid:



$$2C_6H_4\Big\langle\begin{matrix}OH\\NH_2\end{matrix} + 27H_2SO_4 =$$

$$(NH_4)_2SO_4 + 12CO_2 + 26SO_2 + 3H_2O \quad (3)$$

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[1] Presented at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 2 to 6, 1919.

[2] Lunge, "Technical Methods of Chemical Analysis," **1**, Part 1, pp. 309–11; Fresenius-Cohn, p. 573; Sutton, "Volumetric Analysis," Third Edition, p. 100.

[3] Lunge, *Loc. cit.*

[4] Scott, "Standard Methods of Chemical Analysis," p. 306.

[5] Wiley, "Principles and Practice of Agr. Anal.," **2**, p. 397.

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[1] Scott, *Loc. cit.*, p. 303.

[2] *Proc. 8th Intern. Congr. Appl. Chem.*, **1**, 19.

Reaction 3 is completed by adding mercury as in the Modified Kjeldahl method or potassium sulfate as in the Modified Gunning or by adding both as in the Modified Kjeldahl-Gunning method.

The four important considerations in the process of analysis by the Modified Kjeldahl-Gunning method are as follows: Solution, reduction, digestion, and proportion of reagents.

SOLUTION—The sample of nitrate must be dissolved in the salicyl-sulfonic acid (salicylic acid dissolved in sulfuric acid) before the reduction is begun. As usually accomplished this solution is a slow process requiring from one-half hour to a day or more with frequent shaking. It has been generally believed that this must be done in the cold and some have even kept the flasks cooled with ice water, hoping thereby to avoid loss of nitrogen as nitric acid. The loss of time occasioned by dissolving the sample, even at room temperature, was so great as to make burdensome the amount of work contemplated. Attempts were made to hasten solution by heating gently, when it developed that solution could be effected very rapidly. The heating may be done by immersing flask in boiling water, or more easily over low flame or electric heater and with frequent shaking, heating the flask not much hotter than the hand can bear. A peculiar hissing sound is observed when the heat is applied, and the solution completed in from one to three minutes without the slightest loss of nitrogen. Results were even more concordant than when allowing to dissolve by long standing at room temperature.

REDUCTION—While zinc dust is used by some analysts for the reduction, the writer has found sodium hyposulfite, "hypo," more convenient and also that it gives more reliable results. This may be due to inexperience with zinc dust, which has given low results. The results reported herein were obtained using hypo. The hypo is added as soon as solution is complete to the warm solution and, after shaking, the flask is warmed gently at first until frothing ceases (about 5 min.), when the mercury and potassium sulfate are added and the heat increased. This manner of reduction is simple, rapid, and complete in a very short time.

DIGESTION—The important considerations in this stage are the length of the digestion period, the rate of boiling or amount of heat applied, and the amounts of reagents employed, as will be noted from a study of Tables I to IV. It is noted that at least 45 cc. to 50 cc. salicyl-sulfonic acid are required for 0.8517 g. sodium nitrate and that as much as 4 to 8 hrs. at gentle boil and using 5 g. potassium sulfate and 0.5 g. mercury are required for digestion, as per Reaction 3 above. It is noted further that by using 10 g. potassium sulfate, 1 g. mercury, digesting at a brisk boil 1 hr. after solution had become clear, is sufficient.

PROPORTION OF REAGENTS—From Reaction 1 it may be determined that 1 g. sodium nitrate requires 1.64 g. salicylic acid. In various textbooks it is stated that from 0.25 to 5 g. nitrate may be taken with 30 to 35 cc. sulfuric acid and 2 g. salicylic acid. From this it may be understood why some analysts have not obtained concordant and correct results on account of failure to use the correct proportion of reagents.

In 1911, the Committee on Nitrogen, Division of Fertilizer Chemists, AMERICAN CHEMICAL SOCIETY, received reports from fifteen analysts from coöperative work on a sample of nitrate of soda sent out by the committee, and the committee in its report noted the tendency to higher results when a 0.25 g. sample of nitrate was used than when using larger quantities. This is due to the fact that a more nearly correct proportion of reagents was employed when the smaller sample was used. Hardly any two analysts described the same details of analysis.

TABLE I

REAGENTS: 0.8517 g. sodium nitrate 1 (20.01 per cent NH_3—accepted value); 50 cc. salicyl-sulfonic acid (containing 2 g. salicylic acid) warming to effect solution; 5 g. hypo; 5 to 6 g. potassium sulfate; 0.5 g. mercury; 1 g. sodium sulfide, etc.

No. determinations..	4	2	7	8	15	7	15	...
Digestion after solution is clear, boiling gently, hrs.[1]......	1	1.5	2	3	4	5	6	8
Max. result, per cent	19.86	19.95	19.99	20.02	20.02	20.02	20.04	...
Min. result, per cent	19.81	19.91	19.81	19.86	19.92	19.93	19.91	...
Av. of all, per cent..	19.84	19.93	19.90	19.95	19.97	19.97	20.00	...
Same as Above, but Added 10 g. Potassium Sulfate								
No. determinations..	25	...	14	17	27	...	8	7
Max. result, per cent	20.04	...	20.05	20.01	20.03	...	20.02	20.06
Min. result, per cent	19.81	...	19.91	19.86	19.93	...	19.96	19.92
Av. of all, per cent..	19.95	...	19.97	19.95	19.99	...	20.00	20.01
Same, but after Adding 10 g. Potassium Sulfate and 0.5 g. Mercury at Brisk Boil[2]								
No. determinations..	...	...	4	4	15	5	...	...
Digestion, hrs.......	...	...	0.25	0.5	1.0	1.5	...	...
Max. result, per cent	...	...	19.95	19.98	20.03	20.05	...	...
Min. result, per cent	...	...	19.88	19.93	19.98	19.96	...	...
Av. of all, per cent..	...	...	19.92	19.95	20.01	20.00	...	...

[1] By "gentle boil" is meant sufficient heat to keep contents of flask just boiling.

[2] By "brisk boil" is meant sufficient heat to keep contents of flask boiling briskly, and to keep the neck of the flask washed down by the sulfuric acid condensing therein.

Probably most analysts use not over 0.5 g. sample of sodium nitrate for the analysis, and from other results obtained it was found that for 0.5 g. sample 35 cc. of salicyl-sulfonic acid, containing 1 g. salicylic acid, 5 g. hypo, 5 to 6 g. potassium sulfate, 0.5 g. mercury, 1 g. sodium sulfide, and digesting for 1 hr. after clear at a slow boil, gave correct results. It thus appears that the proportion of reagents is very important. It was found further that 1 g. sample of sodium nitrate could be used with the same proportion of reagents as used in this work with 0.8517 g. Table III shows that at least 45 cc., and preferably 50 cc., salicyl-sulfonic acid are required for 0.8517 g. sample, and other reagents used, and Table 4 shows that for 1.7034 g. sample 70 cc. are required. Why it is necessary to use so great an excess of sulfuric acid with increase in sample is not apparent. It is not to prevent loss of ammonia from ammonium sulfate, as was proved by using a sample of pure ammonium sulfate, weighing out 0.4259 g., 0.8517 g., and 1.7034 g. portions, digesting with 25 cc., 30 cc., 35 cc., and 40 cc. sulfuric acid, and adding 10 g. potassium sulfate, 0.5 g. mercury, 1 g. sodium sulfide, 1 g. sugar, etc., and digesting for 2 hrs. after clear at gentle boil. Results were practically the same with all portions and for all amounts of sulfuric acid.

EXPERIMENTAL WORK

The samples used for this experimental work, as reported partly in Tables I to IV, were as follows:

(1) Sodium nitrate 1, a sample of sodium nitrate

TABLE II

REAGENTS: 1.0134 g. potassium nitrate (equivalent to 0.8517 g sodium nitrate); 50 cc. salicyl-sulfonic acid (containing 2 g. salicylic acid) warming to effect solution; 5 g. hypo; 5 to 6 g. potassium sulfate; 0.5 g. mercury; 1 g. sodium sulfide, etc.

No. determinations	6	...	...
Digestion after solution is clear, boiling gently, hrs.	4	6	8
Maximum result, per cent	20.00	...	...
Minimum result, per cent	19.93	...	...
Average of all, per cent	19.98	...	...

Same, but 10 g. Potassium Sulfate

No. determinations	9	8	8
Maximum result, per cent	20.03	20.08	20.03
Minimum result, per cent	19.96	19.93	19.89
Average of all, per cent	19.99	20.01	19.95

Same, but 10 g. Potassium Sulfate, 1 g. Mercury and 2 g. Sodium Sulfide Digesting for One Hour after Clear

	Gentle Boil	Brisk Boil
No. determinations	4	26
Maximum result, per cent	20.07	20.07
Minimum result, per cent	20.00	19.99
Average of all, per cent	20.03	20.036

NOTE—20.038 per cent ammonia is theoretical for pure sodium nitrate.

of high purity, ground and dried at 130° C. The value was accepted as 20.01 per cent ammonia, being the actual result obtained as shown in tables and by comparison with the sample of potassium nitrate.

(2) Potassium nitrate of high purity was recrystallized twice from water, dried at 100° C. and finally at 210° C. This was found free from sulfate, chloride, etc., prepared as per Scott.[1] In using this sample 1.0134 g., equivalent to 0.8517 g. sodium nitrate, were used and results calculated as if pure sodium nitrate was used, containing 20.038 per cent ammonia.

As some laboratories use copper sulfate instead of mercury, some determinations were made using 0.5 g. copper sulfate, but the few results obtained were practically the same though slightly less concordant. The same applies when using 0.5 g. each of mercury and copper sulfate. Copper sulfate offers no advantage over mercury and seems slower in action. Sodium sulfate was found to give the same results as when potassium sulfate was used. The effect of sodium chloride was noted by adding from 0.1 g. to 0.5 g. sodium chloride without effect on the accuracy of the method.

The effect of using moist samples was noted by adding from 0.1 cc. to 0.5 cc. water without affecting the results. At times, however, adding the salicyl-sulfonic acid to moist samples has caused some heating and puffs of nitric acid could be noted, so dry samples are preferable. If not dry the sample may be dried after weighing, except for the difficulty of weighing a moist sample, by rotating flask over a low heat.

The details of analysis for samples of nitrate which give correct results are as follows:

REAGENTS

1—Salicyl-sulfonic acid: 40 g. salicylic acid are made up to one liter with concentrated sulfuric acid

2—Sodium hyposulfite (hypo): Commercial photographic, pea-size

3—Potassium, or sodium, sulfate, preferably dry powder

4—Metallic mercury (or mercuric oxide)

5—Caustic soda: Dissolve 30 lbs. commercial caustic soda in about 2.5 gal. water, let settle, siphon off the clear solution. This strong caustic soda is practically free from carbonate

6—Sodium sulfide: Dissolve 100 g. fused sodium sulfide[2] in water and dilute to 1,000 cc.

7—Pure granulated, or 20 to 30 mesh zinc: Pure zinc is essential as impure zinc reacts so actively with the NaOH that the rapid evolution of hydrogen carries over by entrainment some free alkali, even when using the Hopkins connecting bulb. This causes a variable blank. The Davisson[1] bulb will prevent this entrainment

8—0.5 *N* sulfuric acid solution

9—0.25 *N* or 0.1 *N* NaOH solution

10—Sodium alizarin sulfonate: 2 g. in 100 cc. water.

METHOD

Transfer 0.8517 g. $NaNO_3$ (one gram may be used if desired) preferably to a 650 cc. Pyrex Kjeldahl flask, add 50 cc. salicyl-sulfonic acid, preferably from a dispensing burette, rinsing down neck of the flask, warm over low heat or in boiling water or steam bath until action begins, shaking frequently until solution is complete, add 5 g. hypo, and heat over low heat until frothing ceases (about 5 min.), then add 10 g. sodium of potassium sulfate, 1 g. mercury, and continue digestion until clear, and for an hour afterwards, boiling briskly; cool, dilute with water to about 400 cc., add a small piece of granulated zinc, or a small pinch of 20 or 30 mesh zinc (0.1 g. is sufficient), 70 to 80 cc. caustic soda in which are dissolved 2 g. of fused sodium sulfide. The ammonia is distilled and collected in 0.5 *N* sulfuric acid. About 150 to 200 cc. distillate are sufficient, requiring about 45 min. Use in receiving flask 21 cc. 0.5 *N* sulfuric acid diluted to 125 to 150 cc. with water and three drops of sodium alizarin sulfonate. The number of cc. 0.5 *N* sulfuric acid neutralized by the ammonia gives per cent of the latter when using 0.8517 g. $NaNO_3$.

TABLE III

REAGENTS: 0.8517 g. sodium nitrate 1 (20.01 per cent NH_3); varying the amount of salicyl-sulfonic acid (containing in each case 2 g. salicylic acid) warming to effect solution; 5 g. hypo; 10 g. potassium sulfate; 1 g. mercury; 2 g. sodium sulfide, etc., digesting at brisk boil for one hour after clear.

No. determinations	3	7	7	15[1]	3
Salicyl-sulfonic acid, cc.	35	40	45	50	55
Maximum result, per cent	19.91	20.00	20.05	20.03	20.03
Minimum result, per cent	19.79	19.92	19.96	19 98	19.99
Average of all, per cent	19.86	19.96	20.00	20.01	20.02

[1] In these 15 determinations only 0.5 g. mercury and 1 g. sodium sulfide were used, but 0.5 g. mercury has been found to give (when using 10 g. potassium sulfate) the same result as 1 g., except the latter amount causes the solution to clear more quickly.

TABLE IV—USING SODIUM NITRATE 1 (20.01 PER CENT NH_3)

1.7034 g. sample; salicyl-sulfonic acid as shown (containing in each case 4 g. salicylic acid); 1 g. sodium sulfide for each 0.5 g. mercury.

	MIXTURE					RESULTS		
Cc. Acid	Hypo G.	K_2SO_4 G.	Mercury G.	DIGESTION	No. of Detns.	Maximum	Minimum	Average
50	6–7	5	0.5	0.5 hr. after clear, gentle boil	4	19.80	19.73	19.78
65	10	10	0.5	4 hrs. after clear, gentle boil	5	19.85	19.79	19.83
	10	10	1.0	1 hr. brisk boil after clear	4	19.95	19.90	19.93
	10	10	1.0	2 hr. brisk boil	5	19.93	19.80	19.86
70	8	3	0.5	4 hrs. after clear, gentle boil	2	20.02	19.97	20.00
	10	5	1.0	1 hr. brisk boil after clear	5	20.02	19.94	20.01
75	10	5	1.0	1 hr. brisk boil after clear	2	19.95	19.95	19.95
80	10	5	1.0	1 hr. brisk boil after clear	3	20.00	19.93	19.96

Run a blank on all reagents and apply the correction thus obtained. With good reagents the blank should not amount to more than 0.10 cc. 0.25 *N* sulfuric acid, or on basis of 0.8517 g. $NaNO_3$ to 0.05 per cent NH_3.

In the course of this work about 150 blanks were made, always running several at a time, and they varied from about 0.25 per cent NH_3 in the early work to 0.05 per cent later when a new lot of sulfuric acid free from nitrogen was secured. Results were the same with the high blank as with the low one, but a low blank is obviously to be desired, and without making the blank allowances results exceeding the theoretical would have been obtained.

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[1] *Loc. cit.*

[2] The sodium sulfide solution can be most conveniently made a part of the water used to dissolve the caustic soda. About 75 to 80 cc. of this caustic is required where 50 cc. sulfuric acid have been used. Two grams sodium sulfide should be used for each test.

[1] THIS JOURNAL, **11** (1919), 465.

COMPARISON OF METHOD

Having developed a method for the accurate determination of nitrate, as ammonia, it was decided to compare it with the West Coast, or Refraction, method. Accordingly, four samples of commercial nitrate, Nos. 36059, 60, 61, and 62, received at our plants at various times, were selected for comparison, and results appear in Tables V and VI. These results only confirm the more elaborate comparison of Mr. W. S. Allen,[1] and show that on one sample the agreement is very close. In another it is very close after making allowance for the potassium nitrate, but in the other two samples correcting for potassium nitrate still leaves a discrepancy of nearly 1.5 per cent $NaNO_3$, indicating that this error is due to other impurities. The West Coast method gives results which are often very deceptive and the buyer may pay for as much as 2 to 3 per cent $NaNO_3$ more than he actually receives.

TABLE V—RESULTS ON SAMPLES BY THE WEST COAST OR REFRACTION METHOD

	36059 Per cent	36060 Per cent	36061 Per cent	36062 Per cent
Insoluble	0.27	0.14	0.16	0.48
NaCl	0.94	2.37	1.69	1.29
Na_2SO_4	0.16	0.22	0.25	0.32
H_2O at 130° C.	0.41	0.55	0.59	0.56
TOTAL	1.78	3.28	2.69	2.65
$NaNO_3$ by difference	98.22	97.62	97.31	97.35
K_2O found	0.34	3.33	3.26	4.26
Equivalent to KNO_3	0.73	7.15	7.00	9.14
Error in $NaNO_3$ due to KNO_3	0.12	1.14	1.12	1.46

TABLE VI—RESULTS ON SAMPLES BY DETERMINATION AS NH_3 BY USING 0.8517 G., 50 CC. SALICYL-SULFONIC ACID, ETC.

	36059 Per cent	36060 Per cent	36061 Per cent	36062 Per cent
	19.69	18.84	18.96	19.22
	19.68	18.89	18.98	19.18
	19.63	18.90	18.95	19.28
	19.69	18.94	18.99	19.22
	19.64	18.86	18.96	19.22
AVERAGE,	19.67	18.89	18.99	19.22
Equivalent to $NaNO_3$	98.17	94.27	94.77	95.92
Error due to West Coast—per cent $NaNO_3$	0.05	2.45	2.54	1.43
Net error as $NaNO_3$ after correcting for per cent KNO_3	0.07	1.31	1.42	0.03

The advantages of the proposed method are: (1) It is convenient, especially fitting the routine of the fertilizer laboratory. A determination may be completed in two and one-half hours; (2) the results are unusually concordant for a material of such high percentage and give theoretical results on pure potassium nitrate.

APPLICATIONS OF METHOD

Following this work and the discovery that a rapid solution of the nitrate in the salicyl-sulfonic mixture by heating gave theoretical results, the question which naturally arises is: Would this same procedure apply to samples of mixed fertilizers containing nitrate? Accordingly a series of samples were prepared as follows:

1—Cured acid phosphate ground to pass 30 mesh.

2—Commercial nitrate of soda, dried, and ground to pass 30 mesh.

3—Tankage ground to pass 30 mesh.

4—Sulfate of potash, dry powder, same as used in ammonia digestions and found free from nitrogen.

The following five mixtures were made up from these samples; the ammonia was not determined on the materials used, but only in the mixture. Mixture 1 serves as a check sample, the amount of acid and tankage remaining the same in all five mixtures. All of these mixtures were made with the utmost care, 200 g. mixtures being made, and all materials weighed on an analytical balance and very carefully mixed.

	(1) Grams	(2) Grams	(3) Grams	(4) Grams	(5) Grams
Acid phosphate	100	100	100	100	100
Tankage	50	50	50	50	50
Nitrate	—	10	20	40	50
Sulfate of potash	50	40	30	10	—

The sample of nitrate of soda was analyzed by the method previously described and found to contain 18.98 per cent ammonia.

The ammonia content of Sample 1 was determined using salicyl-sulfonic acid and reagents as described in Table VII. Various amounts of acid were used but 35 cc. gave the same results as greater amounts, and the ammonia was found to be 2.40 per cent. Samples 2, 3, 4, and 5, therefore, should contain as follows:

(2) 3.35 per cent ammonia (0.95 per cent from nitrate)
(3) 4.30 per cent ammonia (1.90 per cent from nitrate)
(4) 6.20 per cent ammonia (3.80 per cent from nitrate)
(5) 7.15 per cent ammonia (4.75 per cent from nitrate)

From a study of Table VII it will be noted that results are practically theoretical when allowing the sample to remain in the salicyl-sulfonic acid 10 to 15 min. at room temperature with frequent shaking, then adding hypo and proceeding as in the method de-

TABLE VII

1.7034 g. sample; 35 cc. salicyl-sulfonic acid (containing 1 g. salicylic acid); 5 g. hypo; 5 to 6 g. potassium sulfate; 0.5 g. mercury; 1 g. sodium sulfide; etc., digesting 1.5 hrs. after clear at gentle boil

SAMPLE	2	3	4	5
CALCULATED, Per cent	3.35	4.30	6.20	7.15
(1) Standing overnight in salicyl-sulfonic acid at room temperature and shaking several times before adding reagents	3.32	4.30	6.08	6.98
	3.34	4.28	6.07	7.06
	3.37	4.32	6.08	6.96
	3.36	..	6.06	7.07
AVERAGE,	3.36	4.30	6.07	7.02
(2) Standing 10–15 min. after adding salicyl-sulfonic acid at room temperature and shaking several times before adding reagents	3.32	4.28	6.09	7.07
	3.34	4.25	6.17	7.14
	3.34	4.23	6.15	7.09
	3.30	4.23	6.14	6.97
	3.37	4.25	6.15	7.08
	3.32	4.28	6.11	6.97
AVERAGE,	3.33	4.25	6.13	7.05
(3) Same as (2) but stood 1.5 hrs. after adding salicyl-sulfonic acid	3.31	4.27	6.12	7.06
	3.42	4.27	6.13	6.91
AVERAGE,	3.36	4.27	6.13	7.01
Same as Above, but Using 0.8517 g. Sample				
Same as (1) above	3.33	4.27	6.12	..
	3.33	4.34	6.12	..
	3.32	4.36	6.14	..
	3.37	4.24	6.19	..
	..	..	6.13	..
AVERAGE,	3.34	4.30	6.13	..
Same as (2), above	3.33	4.27	6.13	7.14
	3.38	4.27	6.18	7.11
	3.30	4.34	6.18	7.14
	3.32	4.29	6.16	7.18
AVERAGE,	3.33	4.29	6.16	7.14

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[1] *Loc. cit.*

scribed previously. It will be noted that results for Samples 3, 4, and 5 are slightly better when using 0.8517 g. than when using 1.7034 g. It was also found from results not reported, using Sample 5, that using 1.7034 g. sample with 50 cc. salicyl-sulfonic acid (containing 1.5 g. salicylic acid), 5 g. hypo, 5 to 6 g. potassium sulfate, 1 g. mercury, 2 g. sodium sulfide, etc., that the same results were obtained as when using 0.8517 g. with 35 cc. of acid, etc. Here again the proportions of reagents and sample are found to be important and indicate that for samples containing high nitrate content, say, 4 per cent ammonia or over, more correct results may be obtained by using 0.8517 g. sample, as the use of 50 cc. of acid is hardly to be recommended.

Determinations were also made on Samples 2, 3, 4, and 5 by warming after adding the salicyl-sulfonic acid, as described before in case of nitrate, but for all samples the results were slightly lower, amounting from 0.05 per cent to 0.10 per cent ammonia.

SUMMARY

From the foregoing it appears that the best and really most convenient procedure for the determination of total ammonia in fertilizers containing nitrate is as follows:

Weigh 1.7034 g. sample (0.8517 g. in case of mixtures high in nitrate) preferably into a 650 cc. Pyrex Kjeldahl flask, add 35 cc. salicyl-sulfonic acid, containing 1 g. salicylic acid, and after shaking frequently for 15 min. add 5 g. hypo, heat gently until frothing ceases, add 5 g. potassium or sodium sulfate, 0.5 g. mercury, and digest until clear and for 1.5 hrs. or more afterwards, cool, dilute to about 400 cc. and proceed as in case of nitrate samples, using in this case 1 g. sodium sulfide.

Altogether over 1,000 determinations have been made on nitrate samples and about 200 determinations on the four mixed fertilizer samples and the results summarized in the foregoing tables. All determinations have been corrected for ammonia in reagents, by blank determinations run with nearly every set, measuring apparatus carefully calibrated, standard solutions frequently checked and allowance made for change in temperature of these solutions. The 0.5 N sulfuric acid solution was standardized by three methods: (1) By sodium carbonate prepared as per Scott,[1] (2) by acid potassium phthalate prepared and used as described by Dodge,[2] and (3) by determination as barium sulfate, cold precipitation method of Allen and Bishop. The results by the three methods of standardizing agreed closely, and were as follows in order named: 100.20 per cent, 100.13 per cent, and 100.17 per cent 0.2 N, average 100.17 per cent.

The writer hopes that this contribution to the literature for the correct valuation of nitrate and the determination of total nitrogen in samples of fertilizer containing nitrate may be of value to others and serve in some measure toward the adoption of more uniform methods of analysis; also that the West Coast method for valuation of commercial nitrate of soda may be relegated to the obsolete.

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[1] *Loc. cit.*

[2] This Journal, **7** (1915), 29.

A DIRECT METHOD FOR THE DETERMINATION OF RUBBER HYDROCARBON IN RAW AND VULCANIZED RUBBER[1]

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In the fall of 1916 the writers noticed in the literature[2] a number of articles concerning analytical methods for the determination of rubber hydrocarbon in raw and vulcanized rubber, depending upon the bromine absorbed by rubber. A survey of these articles showed that several different types of bromination methods had been proposed, but the results appeared to be very discrepant. The most promising type seemed to be the one involving the addition of a known amount of bromine, dissolved in a suitable organic solvent, such as carbon tetrachloride, to a solution of the rubber in an organic solvent. After the solution had stood for a period of time the unabsorbed or excess bromine was determined by titration, usually by the addition of standard sodium thiosulfate in the presence of KI solution and starch paste.

Inasmuch as this paper will not deal with the structural formula of rubber, the conventional formula $(C_{10}H_{16})_n$ will be used to designate rubber hydrocarbon, with the understanding that this contains $2n$ double bonds. Two types of reaction are possible, involving in the first case, addition, and in the second, substitution, of bromine.

$$(C_{10}H_{16})_n + 2nBr_2 = (C_{10}H_{16}Br_4)_n \qquad (1)$$

$$(C_{10}H_{16})_n + nBr_2 = (C_{10}H_{15}Br)_n + nHBr \qquad (2)$$

In the second reaction it will be noted that *two* atoms of bromine are necessary to substitute *one* atom of hydrogen, thereby producing one formula weight of HBr. Some of the investigators found that substitution occurred, and tried to choose conditions such that substitution would be minimized or entirely prevented.

McIlhiney[3] has shown that in the bromination of unsaturated oils in an organic solvent the bromine not only adds to the double bonds as in Reaction 1 but a considerable amount is substituted as in Reaction 2. Gill[4] states that rosin oil shows a very high substitution.

This paper deals with the application of the McIlhiney method, developed for unsaturated oils, to rubber hydrocarbon. Briefly, it consists in determining by a volumetric method the substitution which does occur under the particular conditions of the analysis in question, and deducting twice the observed substitution from the bromine consumed, which gives a measure of the true bromine addition, from which the rubber hydrocarbon is readily calculated.

EXPERIMENTAL PART—RAW RUBBER

PREPARATION OF PURE RUBBER HYDROCARBON SOLUTION—Plantation pale crêpe was extracted overnight with acetone[5] in the standard extraction apparatus to remove the resins, then carefully dried, dissolved in pure carbon tetrachloride, and finally filtered to remove the proteins and other insoluble matter. The resulting solution of pure rubber hydrocarbon was analyzed by evaporation to determine the total solids present in a known volume, and this known rubber hydrocarbon content was used as a basis of comparison with the calculated figures found by bromine addition as described below.

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[1] Read before the Rubber Division at the St. Louis Meeting, American Chemical Society, April 12-16, 1920.

[2] See Bibliography, p. 676.

[3] *J. Am. Chem. Soc.*, **21** (1899), 1084.

[4] "Oil Analysis," 9th Ed. (Revised), p. 67.

[5] The acetone was allowed to stand with Na_2CO_3 and $CaCl_2$ and then fractionally distilled.

PROCEDURE—To a known volume of the above pure rubber hydrocarbon solution, containing approximately 0.2 g. $(C_{10}H_{16})_n$, a measured volume of bromine in pure carbon tetrachloride corresponding to approximately 150 per cent excess bromine above that necessary for addition was added, and the mixture was allowed to stand in glass-stoppered bottles for varying lengths of time in a dark closet at room temperature. After this exposure to bromination, 10 cc. of a 3 per cent KI solution were added to take up the excess bromine, and the resulting iodine was titrated by means of 0.25 N standard sodium thiosulfate, using starch paste as an indicator. In order to determine the substitution which had occurred, 10 cc. of 5 per cent KIO_3 were now added to convert the equivalent of the HBr into iodine, which was then titrated to a second end-point. A blank was run under the same conditions as the rubber determination in order to determine the bromine added to the rubber analysis, and to eliminate any error caused by impurities in the reagents used. The sample calculation given below indicates the relation of the various readings.

Rubber taken = 0.2000 G. Thiosulfate Solution = 0.235 N
Equivalent Weight of Rubber Hydrocarbon, $(C_{10}H_{16})_n$ = 34

	Cc. Thio.
For blank	70.00
Excess found by first titration	38.00
Consumed	32.00
Twice second titration, (2) (3.5)	7.00
True addition	25.00

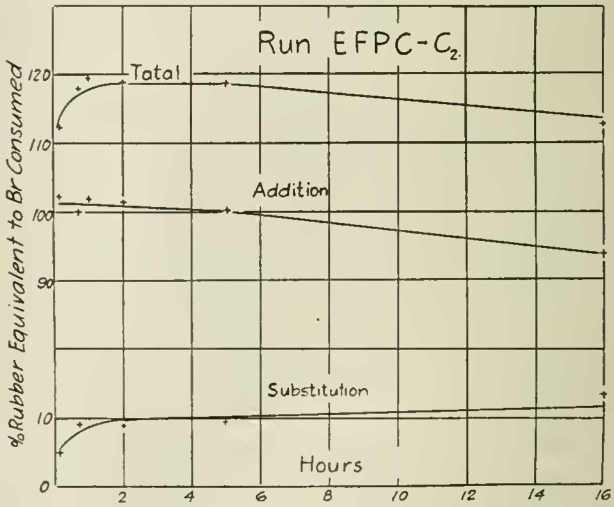
$$\frac{25.00 \times 34 \times 0.235 \times 100}{0.2000 \times 1000} = 100 \text{ per cent theoretical addition}$$

NOTES—In order to avoid loss of bromine vapor upon opening the bottle after the bromination period, the bottle was cooled by immersion for a few minutes in ice water, in the dark, and the KI solution was introduced by means of 1-in. rubber tubing attached to the neck of the bottle and extending up above the stopper.

The carbon tetrachloride was purified by subjecting it to the action of saturated chlorine water for several days in diffused daylight, followed by washing with water and drying with CaO, previous to a distillation in which the fraction boiling within 1° C. of the proper boiling point was taken.

DISCUSSION OF RESULTS—The attached plot shows typical results[1] of runs on extracted, filtered pale crêpe. It will be noticed that the substitution increased with the bromination time, but that the addition followed closely the theoretical 100 per cent line, when the time of exposure was 2 to 4 hrs. The substitution is doubtless a function of the conditions under which the experiment is conducted. For example, it is quite possible that a small amount of water present during the bromination would increase the substitution.

One possible objection to this method is that substitution might continue after the addition of the KI solution. It will be noted that after this time no halogen except iodine is present in the solution, and iodine is known to be much less apt to substitute hydrogen than bromine. Furthermore, if iodine substitution during titration took place before the first end-point no error whatever would be introduced; the effect would be the same as if bromine had been substituted, as the HI so formed would be determined in the second titration and hence an automatic correction would be introduced for this action. However, if iodine substitution took place after the first end-point (by the substitution of iodine produced by the action of KIO_3 on the HI already present) the second titration would be high and the calculated addition would be low, because the addition is obtained by subtracting twice the second titration from the bromine consumed in the first. Furthermore, if at any time HBr splits off from the brominated molecule and this action is not accompanied by further addition, the calculated addition would be low. The results as shown in the attached plot indicate that if such undesirable actions occurred they were negligible in effect.



VULCANIZED RUBBER

The above results have shown the method to be satisfactory for raw rubber; it remained for Sackett and Seltzer[1] to adapt it to vulcanized rubber. Since carbon tetrachloride will not "dissolve" vulcanized rubber, a new "solvent" had to be obtained, and the choice was tetrachlorethane.

In addition to the rubber hydrocarbon, resins, and proteins present in raw rubber, vulcanized rubber may contain fillers and compounding materials, such as mineral oxides or salts, carbon, mineral rubber, organic accelerators, vulcanized oils (factice), free sulfur, and sulfur combined as polyprene disulfide, $(C_{10}H_{16}S_2)_n$.

The acetone extraction of the finely cut sample was made to remove not only resins but also free sulfur and other acetone-soluble materials. The rubber residue was dissolved by refluxing with tetrachlorethane[1] for several hours, diluted to a definite volume with carbon tetrachloride, and allowed to settle, then an aliquot part was pipetted out for bromination as in Brandegee's method. The finely divided fillers were excluded from the aliquot part so taken by placing a wad of cotton in the tip of the pipette, and applying a gentle suction. By this means the troublesome centrifuging procedure for eliminating solid material was avoided.

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[1] Brandegee, 1917. Thesis submitted in partial fulfillment of the requirements for the S.B. degree at the Massachusetts Institute of Technology.

[1] Sackett and Seltzer, 1918. Thesis submitted in partial fulfillment of the requirements for the S.B. degree at the Massachusetts Institute of Technology.

During the course of the experimental work Sackett and Seltzer found that substitution could be reduced practically to zero by titrating the brominated sample in very dim daylight, thus eliminating a difficulty previously met by them in an unstable end-point during the second titration. When the per cent excess bromine above that necessary for addition was small (50 per cent) the results were low; 100 to 150 per cent excess bromine gave the best results.

COMBINED SULFUR PROCEDURE—The combined sulfur was found by evaporating to dryness in a porcelain casserole an aliquot part of the tetrachlorethane solution free from insoluble matter, and determining the sulfur by the method of Davies.[2] This consisted in adding 10 cc. of saturated arsenic acid solution, 10 cc. of fuming nitric acid, and 3 cc. of bromine water, and evaporating to a sirupy consistency. (If all the organic matter is not destroyed, more fuming nitric acid is added, and the mixture again evaporated to a sirupy consistency.) After the addition of a few crystals of potassium chlorate, the solution is evaporated to dryness, heated to boiling with 50 cc. of 10 per cent hydrochloric acid solution, filtered through paper, and diluted to 300 cc. with distilled water in a beaker. The sulfuric acid is precipitated as barium sulfate by the addition of barium chloride, and determined gravimetrically in the usual manner.

CALCULATION OF TOTAL RUBBER HYDROCARBON—The rubber hydrocarbon combined with the sulfur thus found is calculated by multiplying the percentage of sulfur by $\frac{C_{10}H_{16}}{S_2}$, or $\frac{136}{64} = 2.13$.

The total rubber hydrocarbon is calculated by adding the rubber hydrocarbon combined with the sulfur and the uncombined rubber hydrocarbon found from the bromine addition.

PROCEDURE FOR VULCANIZED RUBBER—Extract a weighed sample (approximately 1.5 to 2.0 g.) of vulcanized rubber with acetone for 8 hrs. in the standard extraction apparatus, evaporating the acetone to obtain the percentage of acetone-soluble material.[3] Aspirate CO_2 through the rubber to remove the traces of acetone, reflux 4 hrs. with approximately 100 cc. of tetrachlorethane, cool, and make up to mark in a 250 cc. calibrated flask with carbon tetrachloride. Remove a 25 cc. aliquot portion by applying gentle suction to a pipette containing a small piece of cotton in its tip. Place this sample in a glass-stoppered bottle of 250 to 500 cc. capacity, add from a burette a measured amount of bromine in carbon tetrachloride corresponding to at least 100 per cent excess bromine above that necessary for the addition reaction, insert the stopper tightly, and allow to stand for 3 hrs. in a dark closet. At the end of this time, darken the room, add 10 cc. of 10 per cent KI solution, shake, and titrate rapidly with 0.1 *N* standard sodium thiosulfate, using starch paste as an indicator. As soon as the first end-point has been noted, add 10 cc. of 1 per cent KIO_3 solution, and titrate rapidly to the second end-point with thiosulfate. The titration of a blank run under similar conditions gives the thiosulfate equivalent of the bromine added.

The method of calculation of the results is entirely similar to that used in the case of raw rubber, except that to get total rubber the rubber equivalent to combined sulfur is added to that determined by bromination.

RESULTS

TABLE I—RUBBER HYDROCARBON BY ADDITION

SAMPLE	INDIVIDUAL RUNS PER CENT				AVERAGE PER CENT
A	86.2	86.6	86.2	83.8	85.5
B	63.5	66.5	..	..	65.0
C	56.6	52.6	52.7	50.7	53.2
D	54.2	55.0	53.5	55.0	54.4
E	45.4	45.2	..	..	45.3
F	80.5	81.9	74.9	74.7	78.0

The final analyses are summarized in Table II.

TABLE II

Sample	Acetone Extract Per cent	Nature of Compounding Material	Combined Sulfur Per cent	Rubber Equivalent of Combined Sulfur Per cent	Uncombined Rubber (by Bromination) Per cent	Total Rubber (by Analysis) Per cent	Total Rubber Known Composition Per cent	Error in Total Rubber Hydrocarbon Per cent
A	3.46	None	3.4	7.2	85.5	92.7	93.7	—1.05
B	1.90	Litharge	3.1	6.6	65.0	71.6	75	—3.4
C	2.33	Zinc oxide	3.3	7.0	53.2	60.2	60	+0.2
D	2.33	Sublimed lead	1.6	3.5	54.4	57.9	60	—2.1
E	..	Zinc oxide and organic accelerator	1.1	2.4	45.3	47.7	48	—0.4
F	..	Mineral rubber and accelerator	2.16	4.6	78.0	82.6	80.5	+2.1

Table II compares the percentages of total rubber hydrocarbon as found by analysis with the known figures for rubber content supplied by the compounders of the samples. In no case did the analyst have any information as to the composition of the samples. The analytical figures average low, as they should do because of the resin and protein content of the raw rubber. The analytical results are, however, probably high for true rubber hydrocarbon, because any sulfur combining with resin, protein, or accelerator to give a product insoluble in acetone but soluble in tetrachlorethane is figured over to its equivalent of rubber, and, further, any sulfur substituting in rubber hydrocarbon itself will increase the results. These factors are probably negligible, except for sulfur combined with artificial accelerators. Any unsaturated organic material insoluble in acetone but dissolved by tetrachlorethane will also increase the analytical results. This is probably a cause of the high figures in the presence of mineral rubber. Few compounding materials are sufficiently unsaturated, however, to be serious in this regard.

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[1] This solvent was purified in the same manner as the carbon tetrachloride.

[2] *Chemist-Analyst*, **15** (1915), 4.

[3] In case "factice" (vulcanized oil) is present, it should be removed by treatment in the usual manner by extraction with alcoholic potash. This treatment was unnecessary for the samples used.

It is believed that this procedure is by far the simplest and most accurate direct estimation of the rubber content of vulcanized articles. It should prove especially useful in the evaluation of shoddies, because it shows the extent to which the unsaturation of the rubber has disappeared, due to previous vulcanizations.

Within the experimental error, the results prove that rubber hydrocarbon is unsaturated to an amount equivalent to four atoms of bromine for each $C_{10}H_{16}$, and further that "combined" sulfur reduces this unsaturation by two bromine atoms for each sulfur combined. These facts seem incompatible with any theory other than that the sulfur taken up by rubber on vulcanization is chemically combined.

SUMMARY

I—Working with a filtered carbon tetrachloride solution of acetone-extracted plantation pale crêpe, it has been shown by a volumetric method involving a double titration that the bromine consumption, corrected for the observed substitution, is a true measure of the actual amount of pure rubber hydrocarbon known to be present. Although the amount of substitution increases with the length of the bromination period, the addition corresponds quantitatively to the actual amount of pure rubber hydrocarbon present, when the bromination time is from 2 to 4 hrs.

II—Experimental data are given to show that the actual per cent of $(C_{10}H_{16})_n$ in vulcanized soft rubber can be determined by a volumetric bromination method herein described, involving a second titration to correct for the substitution which accompanies the particular analysis; by titrating in dim daylight, this substitution correction can be made very small.

III—Tetrachlorethane is a suitable "solvent" for the soft vulcanized rubber goods used.

IV—Experimental data shows that the so-called "combined sulfur" in soft vulcanized rubber is actually combined with the double bonds of the rubber hydrocarbon.

ACKNOWLEDGMENT

The writers desire to express their appreciation of the coöperation of the Chemical Department of the Goodyear Tire & Rubber Company, in preparing samples of known rubber content, and their indebtedness to Messrs. Brandegee, Sackett and Seltzer for developing the analytical procedures and making most of the analyses.

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Caspari, "Bromination of Vulcanized Rubber," *Chem. Abs.*, **6** (1912), 162.

W. Esch "The Analysis of Vulcanized Rubber by the Bromine Method," *Chem. Abs.*, 6 (1912), 806.

T. Budde, "A New Method of Determining the Combined Sulfur in Vulcanized Rubber," *Chem. Abs.*, **3** (1909), 1936.

W. Vaubel, "Contribution to the Bromide Method for the Determination of Rubber," *Chem. Abs.*, **7** (1913), 275.

W. Schmitz, "The Direct Volumetric Estimation of Rubber by Bromine, *Chem. Abs.*, **7** (1913), 4084.

G. Fendler and O. Kuhn, "New Researches on Rubber," *Chem. Abs.*, **2** (1908), 593.

G. Huebner, "Concerning Hard Vulcanized Rubber," *Chem. Abs.*, **4** (1910), 1550.

B. D. Porritt, "The Chemistry of Rubber," *Chemical Monograph*, No. 111, New York.

(Many articles discussing methods, including minor modifications of the same, proposed by the above writers have been omitted from this list.)

METHOD FOR THE DETERMINATION OF THIOCYANATES IN AMMONIACAL LIQUOR AND WASTE LIQUOR FROM AMMONIA STILLS IN THE BY-PRODUCT COKING INDUSTRY

By Joseph A. Shaw

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Received January 8, 1920

To 500 cc. of ammoniacal liquor are added 3 to 5 g. of ferrous sulfate in water solution and about 100 cc. of a 10 per cent sodium hydroxide solution. This is stirred thoroughly and allowed to stand overnight. It is then filtered with gentle suction and washed with cold water containing about 30 g. of sodium hydroxide per liter. The long standing in alkaline solution is necessary in order that the insoluble organic matter may be removed thoroughly from the solution. If this is not done it will continue to settle out from time to time and is liable to cause the analyst to be doubtful of the sharpness of some of his reactions.[1]

By this procedure organic and inorganic material insoluble in alkalies and the sulfides have been removed from the sample and the cyanides changed to ferrocyanides. The alkaline solution is heated to 60° C., made slightly acid with dilute sulfuric acid, and the ferrocyanides precipitated with a slight excess of a 10 per cent ferric chloride solution. After standing a short time the Prussian blue, together with a considerable sludge insoluble in acid solution, is filtered off on a filter similar to the one used to filter the sulfide sludge. The residue may be used to determine total cyanogen after having been washed with a 5 per cent solution of sulfuric acid containing 5 per cent by weight of sodium sulfate.

The filtrate is now made to a definite volume and one-tenth aliquot parts taken. These are heated to 70° C., about 15 cc. of 1 : 4 sulfuric acid added, followed by a decided excess of sodium acid sulfite solution, and the thiocyanate precipitated with a hot 10 per cent solution of copper sulfate. After standing 10 min. the CuCNS is filtered off through a Gooch crucible, the bottom of which is covered with a circle of filter paper, followed by a layer of paper pulp which is in turn partly covered by a small piece of filter paper. Too long standing previous to filtering is to be avoided as it increases the tendency of the CuCNS to pass through the filter as a colloid. The impure CuCNS is washed with hot water of about the same temperature as the original solution which was filtered. Since a little CuCNS sometimes passes through the filter in the colloidal form, the filtrate, if clear, should be removed and discarded as soon as the last of the liquid has been poured through the filter. If a little of the precipitate now passes through the filter upon washing, a quantity of paper pulp may be added to it and the wash water refiltered through an ordinary paper filter, washed with hot water, and combined with the major portion of the CuCNS precipitate.

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[1] It is necessary to use a special filter for the removal of the sludge from the solution mentioned above. This filter is made by placing a perforated porcelain plate in a funnel attached to a filter flask and covering it with a piece of oversized filter paper. When this is drawn into place by the suction a thin layer of asbestos pulp is poured on the filter and another piece of filter paper cut considerably under size is placed on top. After a little washing and adjustment the filter is ready to use. Or if desired and available a small Büchner funnel may be used instead of the funnel and porcelain plate employed above.

The residue, consisting chiefly of paper pulp and CuCNS, is treated with 25 cc. of *N* sodium hydroxide, a little bromine water is added to oxidize the copper, and after a few minutes the paper pulp is filtered off and thoroughly washed with hot water. A little more bromine water is added to the alkaline solution and it is digested at the boiling point for one hour. It is made slightly acid with hydrochloric acid, the bromine boiled off, and the solution taken to dryness. The dry residue is taken up with hot water containing a little HCl and filtered from silica. The sulfur present originally in the CuCNS is the only sulfur now left in the solution and it is entirely in the form of sulfate. This may now be precipitated with barium chloride and determined in the usual manner and the thiocyanate calculated.

For the purpose of checking the method, the thiocyanate content of the liquor was determined by the above method and also the thiocyanate content of the liquor to which a known amount of potassium thiocyanate had been added. The results indicated that thiocyanate in ammoniacal liquor can be determined by this method to within 0.01 g. per liter.

Aside from the exercise of a little technique in filtering, the analysis proceeds quite nicely.

VOLUMETRIC METHOD FOR THE DETERMINATION OF DIASTATIC CAPACITY

By J. T. Flohil

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Received January 16, 1920

A 5 per cent malt solution is prepared according to Lintner.[1] One cc. of the extract is introduced into 100 cc. of a 2 per cent soluble starch solution in a 200 cc. flask, left to act for exactly one hour at 20° C., then treated with 10 cc. of 0.1 *N* sodium hydroxide to stop the diastatic action, and diluted with water to the 200 cc. mark.

Twenty-five cc. of this solution are transferred to a 300 cc. Erlenmeyer flask, exactly 10 cc. each of Fehling's Solutions I and II added, and the volume brought up to 50 cc. with 5 cc. water. The mixture is boiled slowly for 2 min., and immediately cooled under the cold water faucet, but not much under 25°. Ten cc. of a 30 per cent potassium iodide solution, or 3 g. potassium iodide and 10 cc. of a 25 per cent sulfuric acid solution, are added successively and the liberated iodine titrated with a 0.1 *N* thiosulfate solution to a creamy yellow color, the soluble starch present serving as an indicator.

CALCULATION

Let p cc. be the amount of thiosulfate used in this titration, n cc. the amount of thiosulfate used in a blank test (25 cc., 5 cc. water, 20 cc. Fehling's solution); then $n - p = m$ is the amount of thiosulfate equivalent to the copper sulfate reduced by the maltose sugar.

According to Lintner, if 1 cc. of a 5 per cent malt infusion in 100 cc. of 2 per cent starch solution produces just enough maltose to reduce 50 cc. of Fehling's solution its strength is 100°. This solution diluted to 200 cc. of 1 per cent starch solution will also reduce 50 cc. of Fehling's solution, and 25 cc. will reduce 6.25 cc. of Fehling's solution. We here assume that the quantity of copper sulfate reduced is proportional to the amount of maltose present, without making an appreciable error.

If 20 cc. of the Fehling's solution is equivalent to n cc. 0.1 *N* thiosulfate, then 1 cc. is equivalent to $n/20$ cc. thiosulfate.

If 25 cc. of the solution mentioned in the beginning of this article reduce Fehling's solution equivalent to 6.25 $n/20$ cc. of thiosulfate, the Lintner value is 100°.

If 25 cc. of the solution reduce Fehling's solution equivalent to m cc. of thiosulfate, its strength is

$$\frac{m}{\frac{6.25\,n}{20}} \times 100 = 320\,\frac{m}{n} \text{ degrees Lintner.}$$

EXAMPLE—In a blank test the amount of iodine set free by the copper sulfate was equivalent to 27.0 cc. 0.1 *N* thiosulfate, or $n = 27.0$.

In the actual test the amount of iodine set free by the copper sulfate was equivalent to 15.0 cc. 0.1 *N* thiosulfate; therefore $m = 27.0 - 15.0 = 12.0$ and the diastatic capacity is 320 12/27 or 142° Lintner.

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[1] *Z. prakt. Chem.*, **1886**, 386.

THE UNIFORM COMPOSITION OF COMMERCIAL "STEARIC" ACIDS, AND ITS EXPLANATION

By Ben H. Nicolet

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Received October 27, 1919

Sometime ago the writer had occasion to make some comparative tests on a number of samples of commercial stearic acids chosen at random. The titers were surprisingly uniform throughout the series and when these were corrected for the small and varying iodine numbers which the different samples showed, the agreement became startling. The maximum variation in the corrected titers for the six samples, coming from five entirely different sources, was less than 0.5°.

Such a finding appeared to demand an explanation, and one is here offered, based on the known series of solid solutions formed in mixtures of stearic and palmitic acids.

The results of interest in the present connection are given in Table I. The samples examined may be described as follows:

(1) Domestic, source unknown
(2) "Best," Celina Stearic Acid Company
(3) "Standard," Emery Candle Company
(4) "Double pressed," Rub-No-More Company
(5) "Triple pressed," Rub-No-More Company
(6) "Finest imported," Dutch

Technical stearic acid is produced by successive pressings of fatty acid mixtures which originally have a considerable content of unsaturated fatty acids. At each pressing, a lower melting fraction is removed, and after two or three pressings little of the unsaturated acids remain, as shown by the iodine numbers found.

Table I—Examination of Commercial "Stearic" Acids

Sample number	1	2	3	4	5	6
Iodine number	1.3	1.6	8.0	4.0	1.9	2.4
Oleic acid (calc. per cent)	1.4	1.8	8.8	4.4	2.1	2.6
Titer[1]	55.2°	55.3°	53.9°	54.3°	55.0°	54.8°
Titer for zero I_2 number (calc.)	55.48°	55.66°	55.66°	55.18°	55.42°	55.32°

[1] The titers calculated for zero iodine number were obtained by adding to the titers found 0.2° for each per cent oleic acid present. This is an approximately correct allowance for small amounts of oleic acid in any stearic-palmitic acid mixture.

The constancy of the titers given in the last line of the table indicates that the ratio of stearic to palmitic acid approaches a definite value as the pressing is continued.

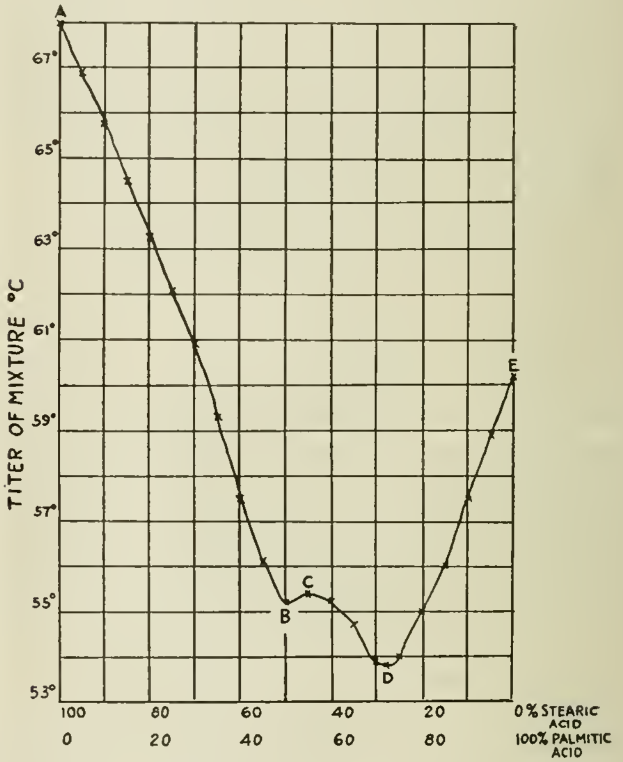
To explain this it is necessary to refer to the curve showing the solidifying points of the system stearic acid–palmitic acid. De Visser[1] and Carlinfanti and Levi-Malvano[2] have drawn such curves and pointed out the relations which they indicate as to the formation of solid solutions. Since titer determinations as ordinarily carried out vary somewhat in principle as well as in practice from the carefully determined solidification points of these authors, a similar curve of titers of mixtures of stearic and palmitic acids is given in the accompanying curve. The values from which this curve is constructed were determined for a different purpose and will be given elsewhere.

From A, the titer of pure stearic acid, the curve falls continuously to B, then with further addition of palmitic acid rises slightly to a maximum at C and then falls to D. From D the curve again rises normally to E, the titer of pure palmitic acid. The curve is thus divided into sections in which the effect of fractional crystallization, either with or without a solvent, will be very different. The pressing to which the acids are subjected is equivalent to a fractional crystallization.

The general laws describing the behavior of solid solutions indicate that a mixture whose composition was represented by any point between B and A would eventually yield pure stearic acid. Similarly, pure palmitic acid would be the end-product from a mixture lying between D and E. On the other hand, a mixture originally represented by a point on the section BD would approach the composition represented by the maximum at C and thereafter show no further separation.

The point C represents a palmitic acid content of 55 per cent, and a titer of 55.4°. This appears to be a rather close description of the "stearic" acids examined. Furthermore, their titers are depressed by successive small additions of palmitic acid. A little stearic acid added lowers the titer, and further additions raise it rather rapidly. The acids have all therefore approximately the composition C, which apparently is represented on the curve with a titer a few tenths of a degree too low.

All the samples examined are thus seen to contain palmitic acid to the extent of 52.5 to 55 per cent of their saturated acids. If the explanation here put forward be accepted, it follows that in the material originally subjected to pressing, the *saturated* acids contained between 50 and 72 per cent palmitic acid.



TITERS OF STEARIC-PALMITIC ACID MIXTURES

Very little is actually known as to the ratio of palmitic to stearic acid in fats and oils. Most of the information on the subject in the literature comes from the work of Hehner and Mitchell[1] on the determination of stearic acid. They report a commercial stearic acid examined by them as having iodine number 2.3, melting point (not titer) 56.2°, and stearic acid 48.7 per cent (the mean of five determinations varying from 47.0 to 50.6 per cent). In view of the uncertainty of their method, these results do not contradict the conclusions here reached.

SUMMARY

Attention is called to the remarkable constancy of the ratio of palmitic to stearic acids in a number of technical "stearic" acids.

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[1] *Rec. trav. chim.*, **17** (1898), 182, 316.

[2] *Gazz. chim. ital.*, [II] **39** (1909), 368.

[1] *Analyst*, **21** (1896), 316.

An explanation of this constancy is offered based on the solid solutions formed between these two acids. This requires that "stearic" acids showing this effect should have as their source acid mixtures, the saturated acids of which contain between 53 and 72 per cent of palmitic acid.

As the explanation given must stand or fall with the necessity of the fulfillment of this condition, and as the writer is not sufficiently familiar with the manufacture of "stearic" acid to know whether in general it is fulfilled, discussion on this point is particularly invited.

LABORATORY AND PLANT

PHOTOBIBLIOGRAPHIC RESEARCH METHODS—THE COMPILATION OF TECHNICAL DATA WITH THE AID OF PHOTOGRAPHY

By Arthur Worischek

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Received May 11, 1920

The methods employed by professional searchers, compilers and "experts in patent causes," although not yet standardized, have nevertheless been very ably described.[1]

The weakest point in any system of searching and collating technical data is the accurate transcription of tabulated matter and the reproduction of illustrations when these occur in the text. In the author's opinion, it should be possible to copy articles, tables, complicated diagrams and even entire chapters of textbooks by means of some cheap and simple process and without causing annoyance to fellow readers or damage to the books consulted. If a journey to a distant library is necessitated it should be possible to so plan the trip that copies of all the data needed in a given investigation may be brought home in a convenient form. A research worker would then be able to compile his own textbook on any given subject and arrange the subject matter to suit his own particular convenience and needs.

The author having had occasion to undertake extensive research searching during the past few months was struck by the lack of any simple method for copying articles and diagrams. Tedious scribbling appears to be the method exclusively employed, with occasional laborious and time-consuming tracing. A search through the literature revealed a number of attempts along this line, all based upon some adaptation of photography.[2]

Microphotographic copying of printed matter was employed for the transmission of intelligence during the siege of Paris in 1870.[3] Despatches were printed on a large sheet of paper which was then microphotographically copied onto a film of collodion. According to Tissandier[4] each page contained some 5,000 letters, equivalent to 300 despatches, and 16 of these pages were copied onto a collodion film 2 in. long and 1 in. wide, weighing less than one grain. These films were transmitted by carrier pigeons and upon arrival at headquarters were placed in a projecting lantern and thrown upon a screen, while a number of copyists or scribes transcribed the despatches.

Fessenden[1] described a method for photographically compiling his own data collection. His method consisted in copying pages of books onto standard sized plates from which standard sized prints could be made, suitable index numbers being marked upon the film before printing. Other workers have also proposed similar schemes and a method was described in 1909[2] in which the book to be copied was placed upon the floor and copied by means of a camera equipped with a reversing mirror and using bromide paper instead of plates. In the "reflection by contact" or "catatype" method[3] a sheet of sensitized paper is placed with its sensitive side in contact with the print to be copied, the light being allowed to pass through the paper. The method does not, however, appear to have come into practical use.

J. L. Mauch[4] has obtained a patent for a "photogenic copying device." He has combined "means for applying a sensitized strip to a surface to be copied with means for projecting light through said strip upon said surface and means to obtain a uniform exposure of said strip." The apparatus is to be held in the hand and "rolled" over the page of a book, etc., the unexposed sensitive paper being drawn from one spool and the exposed paper wound up on another spool. This, therefore, appears to be a mechanically controlled application of the "reflection by contact" method. A patent by H. H. Curtiss[5] relates to a similar device.

Various commercial methods have been proposed for copying directly upon bromide paper without the intermediary of a negative.

A number of years ago there was introduced a commercial bromide paper copying machine known as the "Record Camera,"[6] which was equipped with a

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[1] A. B. Eason, "Sources of Technical Information," *Electrician* (*Lon.*), **82** (1919), 326–7; E. D. Greenman, "Technical Literature and How to Use It," *Special Libraries*, **9** (1918), 89; H. Hibbert, "The Art of Searching Chemical Literature," *Chem. & Met. Eng.*, **20** (1919), 578; W. F. Jacob, "The Technical Library and Its Use," *Polytech. Eng.*, **16** (1916), 36; E. N. Jessop, "German Patent Bibliography," This Journal, **8** (1916), 1053.

[2] For an extensive bibliography on the subject of "Photography in Library Work," see G. A. Evers, *Maandblad voor Bibliotheekwezen* (*'sGravenhage*), **1** (1913), 10, 225.

[3] Dagron, "The Preparation of Microphotographic Despatches on Film," *J. Phot. Soc. London*, **15** (1871), 102; *Brit. J. Phot.*, **18** (1871), 616.

[4] "History and Handbook of Photography," London. Translated by J. Thomson. Low, Marston, Low and Searle, 1876. "Microscopic Despatches during the Siege of Paris," Chap. 6, pp. 234–48.

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[1] "Use of Photography in Data Collections," *Elec. World*, **28** (1896), 222.

[2] "Photographing Rare Books and Manuscripts in Libraries," *Bull. de la Soc. Franc. de Phot.*, [2] **25** (1909), 396.

[3] E. E. Fournier d'Albe, "On Photography by Reflection under Contact," *Sci. Proc. Roy. Dublin Soc.*, (New Series) **12** (1909), 97; G. de Fontenay, "Cataphotography; Reproduction of Documents by Reflection," *Compt. rend.*, **152** (1911), 1055, 1298.

[4] "Photogenic Copying Apparatus," U. S. Patent 1,251,076 (Dec. 25, 1917); *Offi. Gaz. U. S. Pat. Office*, **245** (1917), 894.

[5] "Method and Apparatus for Photography," U. S. Patent 1,007,120 (May 19, 1914); *Offi. Gaz. U. S. Pat. Office*, **202** (1914), 745.

[6] "Making Photographic Copies without a Negative," *Am. Machinist*, [1] **31** (1908), 781; Eastman's "Record Camera."

reversing prism and a magazine containing a roll of bromide paper. Upon development a reversed negative (white on black) was obtained. This machine was followed by the well-known "photostat"[1] which embodies the basic principles of the earlier machine but is equipped with means for immediately developing and fixing the print. The cost of a photostat print ranges from 25 to 35 cents per page. Positives (black on white) are secured by copying a negative print, and enlargements and reductions within the capacity of the machine are readily made. S. C. Williams[2] has discussed the cost of photostat work from a scientific viewpoint, and gives formulas for computing the various elements of expense involved. A comparison of the relative costs of brown prints, blue prints, and photostat copies (on a square foot basis) has been made by the Ordnance Department, U. S. Army.[3] The "rectigraph"[4] and the Powers "cameragraphs" (simplex and duplex)[5] are similar machines, the last mentioned being designed to photograph on both sides of a sheet.

In addition to methods intended purely for the copying of printed matter there has been developed a portable camera for use in reading electric and gas meter indices. This is termed the "factograph" camera[6] and is arranged to carry its own source of illumination in the form of several small battery-operated lamps which are lighted by means of a lever which latter also automatically opens the shutter for any desired length of time. A modification of this camera is termed the "finger-print camera" and is used for keeping uniform-sized finger-print records.

EXPERIMENTAL

The author modified Dagron's microphotographic process by substituting motion picture film for the wet collodion pellicle and an *f* 3.5 anastigmatic lens for the slow doublet of 1870. Textbook and periodical pages were photographed, the process used being essentially the same as that used by the cinema companies in copying titles, telegrams, and letters for incorporation into film plays. It was found possible to enlarge the negative film onto bromide paper up to a certain limit in size, *e. g.*, about 5 by 7 in., and although the image was slightly blurred the outlines of the diagrams could nevertheless be distinguished and could be strengthened by inking in. When the film (both negative and positive) was projected onto a screen the print and diagrams were distinctly readable. Oswald,[7] however, has little faith in the use of cinema film for purposes of direct enlargement.

Reasoning from Simpson's and Dagron's postulates, cited above, there appears to be no reason why entire works like Beilstein could not be photographed onto a continuous film[1] (larger in size than ordinary cinema film if necessary)[2] and projected with a suitable apparatus.

A second series of experiments involved the construction of a portable machine of the "photostat" or "rectigraph" type.

This was accomplished, as shown in Fig. 1, by using an Eastman double-extension bellows, revolving back, 3.25 in. by 4.25 in. Auto-Graflex camera. The advantage of the reflex camera resides in the ease with which focusing may be effected, although any ground-glass focus camera may, of course, be used. The lens was equipped with a photoengraver's reversing prism and a simple type of studio shutter, although the camera's own focal plane shutter could also be used. Eastman "Insurance Bromide" paper, Grade B, was used instead of film, being wound on the regular film spools. An exposure (ordinary daylight) of 15 to 20 sec. at *f* 4.5 to *f* 6.3 produced a perfect miniature "photostat" print. Exposure under one 16 candle-power incandescent lamp, representing ordinary New York library lighting conditions, required about 10 sec. longer. Experiments were made using a 5 by 7 view camera, equally good results being obtained, the detail and sharpness of the prints being remarkable. A whole page of Beilstein when reduced to 3.25 by 4.25 in. in size was as distinctly readable as the original, and when such a small print was recopied and enlarged several times by a regular "photostat" machine its size was restored to that of the original page without any material sacrifice in sharpness of definition.

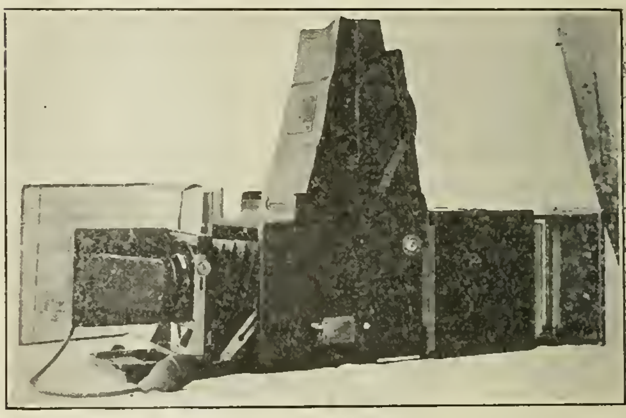

FIG 1—INSTANT-FOCUSING REFLEX CAMERA EQUIPPED WITH PRISM AND LARGE-CAPACITY BROMIDE ROLL HOLDER, SHOWING METHOD OF USE

Such spools of bromide paper when tightly wound so as to fill completely the regular film spools in the case of the camera mentioned above represent 15 to

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[1] L. D. Burlingame, "Photostat and Its Uses," *Machinery*, **21** (1915), 951. J. X. Cohen, "Methods and Cost of Reproducing and Reducing Engineering Drawings," *Eng. & Contr.*, **46** (1916), 198; "New Reproducing Machine of the Commercial Camera Co.," *Iron Trade Rev.*, **66** (1915), 1106.

[2] "Photostatic Reproduction Cost," *Am. Machinist*, **44** (1916), 487.

[3] U. S. Army, Ordnance Dept., "Cost of Photostats, van Dykes, Blue Prints, Compared," *Eng. News-Record*, **82** (1919), 1065.

[4] *Lumière élec*, **25** (1914), 217.

[5] *Eng. Rec.*, **72** (1915), 32; *Iron Age*, **95** (1915), 1122.

[6] "Camera for Reading Meters," *Am. Gas Lt. J.*, **103** (1915), 141; *Machinery*, **22** (1915), 75. Folmer, U. S. Patents 1,139,022, 1,139,023 (May 11, 1915); *Offi. Gaz. U. S. Pat. Office*, **214** (1915), 497.

[7] "The Movie and the Still Picture," *Literary Digest*, July 5, 1919.

[1] Otlet, in 1918, exhibited examples of such work before various American library gatherings.

[2] "Projecting Larger Pictures with the Standard Motion Picture Film," *Phot. J. Am.*, **56** (1919), 180. Standard size of film retained. Film is moved horizontally and picture is as high as the ordinary image is wide and twice as wide as the regular image is high. The greater size of the film permits greater enlargement.

20 exposures, and a dozen or two of such spools are sufficient for copying a book of respectable size.

The development of a roll of 20 exposures is of course an extremely simple matter, requiring but a few minutes, while the developed paper may be accorded much rougher handling than would be withstood by film. It may, for example, be cut and trimmed while still wet, pasted onto sheets and reports while still damp and portions of illustrations may be inked in with waterproof India ink, the rest of the image being bleached out by some suitable means[1] and the "line cuts" so obtained used for reproduction. After the first print is made it may be recopied to produce black-on-white copies or "positives."

It should, of course, be noted that a suitable "head" or starting piece and "tail" or ending piece of non-actinic or "post office" paper must be pasted onto each end of the sensitive strip for the purpose of starting and ending the spool without spoiling the first and last exposures made. It was discovered, however, that simple blackening of both sides of the bromide paper with India ink for a distance of about one foot from each end of the roll served the same purpose. Inasmuch as no black "duplex" backing paper is used with the bromide paper as in the case of film, the number of the exposure must be indicated in some manner. This is readily accomplished by marking the number of the exposure on the back of the paper with the aid of a cardboard template; a rachet-controlled winding jig is also a great aid in rolling up such homemade spools. The numbering and marking of 10 to 100 ft. of bromide paper proved to be somewhat tedious and a solution of the difficulty was found in the use of the magazine film holder corresponding to the Bannister patent.[1]

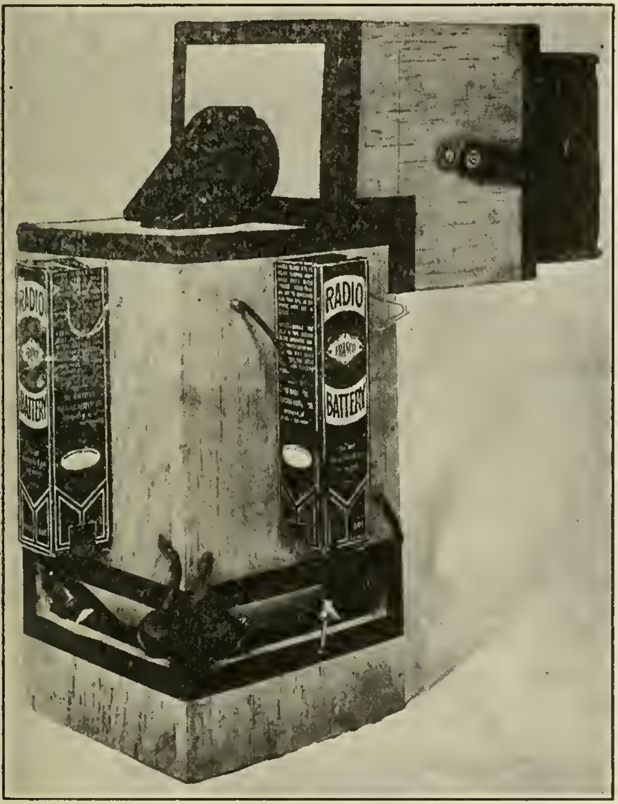

Fig. 2—Self-Illuminated Copying Device Showing Prism, Method of Illumination, and 50 Exposure Bromide Paper Roll Holder

This type of holder was intended for the use of unbacked, un-numbered film, contained on a wooden spool. The film was caused to pass over a large measuring roller carrying two needle points which punched the film at regular intervals corresponding to the size of the picture desired, and the film was prevented from progressing until a suitable release lever had been depressed, or else some external indicating device signaled readiness for a fresh exposure.

Although the apparatus described above is an extremely convenient device for copying books in a distant reference library, it nevertheless appeared possible to render the process of copying more automatic in operation and less dependent upon the operator's judgment regarding sharpness of focus and conditions of illumination. The author, therefore, utilized the principle of the self-illuminated meter reading and finger-print camera mentioned above and built the experimental apparatus depicted in Fig. 2. It was of course necessary to employ the reversing prism used with the reflex camera previously described. This feature makes the apparatus rather awkward and cumbersome, one portion being at right angles to the other, and therefore slightly "top-heavy," but if such a device were to be produced on a commercial scale, a more convenient form, possibly involving the use of a suitable system of reversing mirrors, would undoubtedly be evolved. Pressing the antinous release opens the shutter leading to the lens and prism and simultaneously lights the battery-operated lamps which illuminate the object to be copied. A suitable clockwork or other timing device may, if necessary, be used to actuate the shutter and light-controlling levers so as to insure uniform length of exposure. We would thus have the following practically ideal operating conditions: fixed focus lens, constant intensity of light, uniform time of exposure, and fixed size of object to be copied with a fixed ratio of original to the copy. The apparatus may be built in various forms and sizes, *i. e.*, "page-copier," "diagram-copier," "equation-copier," etc., depending upon the size and use to which the device is to be put. The device might also be so designed as to operate somewhat like a numbering stamp, a simple downward push sufficing to open the shutter and illuminate the object for the required length of time, the mechanism being arranged to automatically supply and wind up the sensitive paper used. H. S. Leach[2] has suggested the advisability of sending expeditions of research workers abroad equipped with photostat machines to copy and bring back material for scholarly study, and the present author would modify the suggestion to the effect that a more portable machine of this type would be a valuable aid to anybody having occasion to make use of a reference library, and the above-proposed small portable machines carried by investigators and translators may very well be used as "feeders" for the large machine in the home plant. The cost of the bromide paper is about $1.75 per 100 ft., and a 100-ft. roll of paper measures only 4.375 in. wide by 4 in. diameter and has a capacity of about 300 exposures. The entire apparatus weighs but a few pounds and does not occupy more than the table space allotted to any one reader or the space occupied by a large dictionary or several volumes of some periodical, and no reasonable objection to its use can be interposed by any librarian, the argument, if any, being on the side of the reader, inasmuch as the book to be copied may be released for issue to another reader in an incredibly short time after "pushing the button."

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[1] E. Senior, "Converting a Photograph into a Line Drawing," *Knowledge*, **11** (1914), 71.

[1] Bannister, "Roll Film Holder," U. S. Patent 316,933 (May 5, 1885); *Offi. Gaz. U. S. Pat. Office*, [1] **31** (1885), 523.

[2] "Photostat as an Aid to Research," *Sci. Am.*, **122** (1920), 276, 291.

CONCLUSION

There is apparently a need for a portable and cheaply operated photographic device for copying illustrations and articles on file in reference libraries—for the purpose of compiling the technical data needed in an investigation. The experiments described indicate that the use and manufacture of such a device are both within the range of commercial possibility. It is believed that a device combining the operating principles of the existing bromide paper copying machines and the self-illuminated meter-reading cameras would prove to be a valuable aid in data compilation, and simple enough in operation for use by non-technical clerical assistants. There appears to be no reason why it should not be possible to simply "push the button—and read the book at home."

POTASH FROM KELP. II—THE EXPERIMENTAL DISTILLATION OF KELP AT LOW TEMPERATURES[1]

By G. C. Spencer

U. S. Kelp Potash Plant, Summerland, California

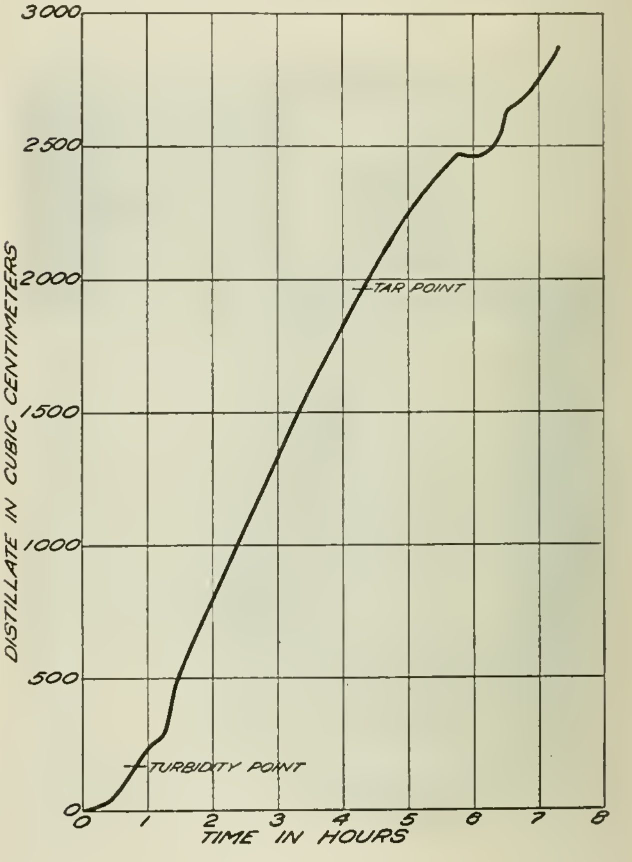
Received March 9, 1920

A study of the experimental, destructive distillation of dried kelp was undertaken to determine whether or not under carefully controlled conditions any relationship could be established between the temperature at which distillation was taking place and the nature of distillation products. The work was done in the Forest Products Laboratory of the U. S. Department of Agriculture, Madison, Wis., in order that the apparatus and technique developed there in the destructive distillation of wood might be available for the research in hand.[2]

Kelp was distilled in an oil-jacketed retort which was built for experimental wood distillation, which has been fully described and illustrated by L. F. Hawley and R. C. Palmer.[3] While this retort was adapted for wood distillation, experience showed that it was not suitable for kelp. However, an interesting collection of data was obtained which is summarized in the paragraphs which follow.

Reference to the specimen log of a distillation run which is here reproduced, as well as a glance at the composite time-distillate curve, will show how the high moisture content of the dried kelp prevents a rapid rise of temperature when the kelp starts to distil. This gradual expulsion of water vapor with its accompanying organic matter undoubtedly tells a story of the volatile kelp constituents that the more rapid heating in a much hotter retort would fail to do.

The retort was preheated by lighting the gas flames of the retort the evening before the run was to be made.



Composite Time-Temperature Curve of Kelp Distillation in Oil-Jacketed Retort Representing Runs 2, 3, 5, 6, and 7

The kelp was charged into the retort in a cylindrical iron cage 3 ft. long and 1 ft. in diameter, inside dimensions. This cage was lined with heavy wire netting preparatory to distilling the dried kelp, and two partitions of the same material were set lengthwise in the middle of the cylinder to provide an air space for the escape of vapors from the middle of the kelp charge.

Sixteen distillations of kelp (average weight of charge 30.2 lbs.) were made in this manner. The first runnings of distillate were always clear and of a bright green color. This condition continued with only a slight increase in density until a temperature, usually above 150° C., was reached, when a turbidity became noticeable in the liquid, which also changed from green to amber. This turbidity indicated a change in the nature of the distillate and the first distillation cut was accordingly made at this point. As the distillation progressed the turbidity increased until a light brown flocculent precipitate separated, which gradually settled out.

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[1] The first paper of this series, entitled "The Experimental Plant of the U. S. Department of Agriculture," by J. W. Turrentine and Paul S. Shoaff, appeared in This Journal, **11** (1919), 864.

[2] Acknowledgments are due to Director Winslow, to Drs. Hawley, Mahood, and others at the Forest Products Laboratory for assistance and courtesies extended, and to Prof. O. L. Kowalke of the University of Wisconsin for the use of laboratory space and apparatus for supplementary work.

[3] "Yields from the Destructive Distillation of Certain Hardwoods," U. S. Dept. of Agr., *Bulletin* **129**.

Experience showed that the next cut should logically be made at the temperature where the tar commenced to come over, but for convenience two and sometimes three fractions were taken before this point was reached. The density of the liquids increased from approximately 1.01 to 1.065, and the amounts of dissolved substances also increased as long as the aqueous distillate continued to flow. It can be seen that the liquor driven off up to the point indicated as turbidity is mostly water. The amount of dissolved material in this fraction is necessarily low, and in all probability this turbidity point represents the first stage of the cellular decomposition. There was at no time any evidence of an exothermic reaction.

Reference to the time-distillate curve will show that, from the point where the first turbidity appears to that where the tar begins to flow, the distillation rate is pictured by a nearly straight line. Above the "tar point" the curve begins to bend and the volume of distillate decreases. The nearly straight line may indicate the passing over of some substance of nearly constant composition, and this belief is substantiated by the isolation of the glycerol-like liquid which will be described in another paper.[1]

The tarry substances were emulsified with an approximately equal quantity of the aqueous distillate and consequently always floated on the watery layer. A sharp separation was impossible, however, since the tar showed a strong tendency to adhere to the glass of the cylinder or of the separatory funnel and to conceal the actual amounts of water and tar.

When kelp is distilled at high temperatures the liberated gas is always combustible. This gas has never been analyzed, but its calorific power has been determined and found to be sufficient for use as a fuel.[2] Such gas, if properly applied, would go far toward reducing fuel costs in a kelp plant.

Samples of gas from the low temperature distillations were analyzed and tested but in no case were the evolved gases inflammable.

The following analyses of gas fractions show that the composition of the gases evolved at different temperatures is nearly the same:

ANALYSES OF GAS FRACTIONS

	131°–135° Per cent	163°–167° Per cent	226°–229° Per cent	271°–275° Per cent
CO_2	80.5	85.5	85.0	82.8
O_2	0.0	0.0	0.0	0.6
CO	11.3	10.3	11.4	10.2

The residual gases were in each case mixed with an excess of air in an explosion pipette but in no case was there a contraction of volume.

The last distillation of kelp that was made in the oil-jacketed retort was modified by mixing 24.1 lbs. of kelp with 5 lbs. of quicklime and carrying out the distillation like those preceding. The aqueous distillate differed from those of the former runs by being alkaline, although at no stage was there any odor of ammonia.

Two gas fractions were taken at 158° to 173° and 255° to 260°, respectively. They differed in composition from those described above in containing less carbon dioxide, which was kept back by the lime, and more carbon monoxide, which would naturally be higher in percentage under such circumstances. No advantage was apparent from mixing lime with the kelp charge.

IGNITION OF CHAR 15 IN A CLOSED RETORT

Inasmuch as none of the charcoal produced in the oil-jacketed retort had been heated sufficiently to remove all of its volatile matter, a portion of the charcoal from Run 15 was heated in an iron retort to as high a temperature as could be attained by a flat burner and a Meker burner together. The retort was set in a holder that prevented air currents from interfering with the flames, but even with this advantage the retort did not appear to be heated to redness. Three and three-tenths pounds (1.5 kg.) of No. 15 char were heated for an hour and a quarter. The retort was not entirely tight and a little of the gas was lost by leakage. The first drop of distillate appeared when the off-take temperature was 98° C. At the same time white vapors began to come over through the condenser. After 40 min. the temperature of the distillate had risen to 101° C. At this temperature the aqueous distillate was brown in color and a dark-colored oil floated thereon. A flocculent precipitate appeared in the watery distillate. When the char had been heated an hour the white vapors stopped coming over, and the temperature rose to 109° C. After this the off-take temperature dropped to 80° C. and no more distillate came. The watery distillate contained ammonium salts.

Weight of char after igoiting	**3.01 lbs.**	**(1.36 kg.)**
Total weight of distillate	**54.2 g.**	**(3.6 per cent)**
Weight of tar	**11.5 g.**	
Weight of water	**42.7 g.**	

This experiment shows that the charcoal produced in the oil-jacketed retort still contains about 9 per cent of volatile matter, which renders it unfit for many purposes. For instance, its aqueous extract is brown in color when it should be water-white, and it is furthermore not sufficiently ignited to be a good filtering medium or absorbent. The residual charcoal from this ignition, on the other hand, is jet-black and its water extract is free from any color whatsoever.

In June 1918 about 10 lbs. of unleached kelp char from Run 6 were forwarded to Dr. F. W. Zerban, of the Louisiana State Sugar Experiment Station at New Orleans, La. Dr. Zerban reignited this char in a closed iron container and leached the residue with water and acid, then made tests on the resulting charcoal to determine its value as a decolorizing agent for sugar solution.[1]

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[1] "The Preliminary Examination of Kelp Distillates."

[2] J. W. Turrentine, "Note on the Distillation of Kelp," *Proc. 8th Intern. Congr. Appl. Chem.*, **15**, 313.

[1] F. W. Zerban and E. C. Freeland, THIS JOURNAL, **10** (1918), 812.

The kelp char made in the oil-jacketed retort did not prove as satisfactory as those originally prepared at higher temperatures.

In the specimen distillation log that follows, the column named "middle temperature," indicates the temperature at the center of the kelp charge, while "maximum temperature" refers to the oil bath surrounding the retort.

DISTILLATION OF KELP

Log of Run 7, May 17, 1918

CONDITIONS: Retort previously heated to 220° C. Strongly heated at first

Time A.M.	Middle Temp. ° C.	Max. Temp. ° C.	Total Distillate Cc.	REMARKS
8:20	140	182	...	Charged retort
8:35	104	175	...	Distillation commences but soon stops
8:45	102	187	...	Minimum temperature
9:00	114	211	...	
9:02	118	215	...	Distillation recommences
9:15	134	231	36.5	
9:30	148	244	97	Clear, green
9:45	158	260	177.5	
10:00	170	273	190.5	Becoming turbid. Fraction 104°-170°, 497 g
10:15	180	285	191	Flaky precipitate
10:30	191	296	184.5	
10:45	201	305	183	
11:00	213	319	188	Fraction 170°-213°, 745 g.
11:15	225	333	185	
11:30	231	340	173	
11:45	247	345	166	Reduced flame[1]
12:00	256	350	144	Tar coming over. Fraction 213°-256°, 668 g.
P.M.				
12:15	267	352	162	
12:30	273	353	119	Tar, 19 g.
12:45	281	354	136	
1:00	289	354	115	
1:15	295	355	109	Water fraction 256°-295°, 530 g. Tar, 50 g.
1:30	300	355	87	
1:45	304	352	73	
2:00	308	350	59	Tar, 55 g.
2:15	310	346	48	
2:30	311	345	43	Tar, 29 g.
2:45	313	350	43.5	Shut off gas. Water fraction, including drip next morning, 373 g.
3:00	317	352	34	
3:30	320	...	...	Tar, 71 g. Total weight of tar, 224 g. (1.4 per cent)

[1] There are two kinds of tar oil: the first that comes over is dark brown with a penetrating though faint odor resembling an essential oil or certain ketones; the second is blacker and has a more unpleasant odor.

RESULTS OF RUN 7

Weight of kelp distilled.................	27.5 lbs.	
Weight of basket and kelp after heating...	107.6 lbs.	
Tare.................................	90.0 lbs	
Residual kelp (non-volatile).............	17.6 lbs.	(64%)
Loss by heating (total volatile)...........	9.9 lbs.	(36%)
Weight of charge.......................	12,500 g.	
Total weight of liquid distillate..........	3,042 g.	(24.3%)
Gaseous distillate......................	....	(11.7%)

ANALYSES OF WATER CUTS LOG 7

Fraction Degrees	Specific Gravity	Solids in 10 Cc. Grams
104-170	1.007	0.1699
170-213	1.013	0.2687
213-256	1.032	0.9159
256-295	1.050	1.5961
295-320	1.063	2.4833

SUMMARY

Sixteen distillations of dried kelp were made in an oil-jacketed wood retort at temperatures not exceeding 320° C. These yielded aqueous liquor, tar, and a noninflammable gas. The residual charcoal was insufficiently heated either for a good extraction of potash or for use as a filtering medium. This work has demonstrated the necessity for distilling kelp at a much higher temperature.

TAR-STILL OPERATION IN HARDWOOD DISTILLATION PLANTS

By L. F. Hawley and H. N. Calderwood, Jr.

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Received February 21, 1920

Sometime ago the authors carried on efficiency studies at several wood-distillation plants with the purpose of preparing a standard set of directions for the use of the refinery foremen and stillmen. The results of the work on the operation of the tar still were of special interest. Since these results are directly applicable to the tar-still operations of many other wood-distillation plants, it was decided to publish them.

The operation carried out in the tar still is for the purpose of recovering the acetic acid that remains in the settled tar after the pyroligneous acid has been removed. In general, the method consists of heating the tar by means of steam in closed coils until the water is driven off, and then, while keeping the closed coils still in use, blowing live steam through the charge.[1] It is obvious that the most desirable conditions for running a tar still are those under which the most acetic acid may be produced in the shortest time and with the greatest degree of concentration. The best conditions for this distillation with respect to speed, length of time, and pressure of steam in the closed coils, have never been determined, and the commercial practice varies greatly.

EFFECT OF SPEED OF DISTILLATION

Two test runs were made with a charge of 510 gal. of tar in a depth of 40 in. The conditions were the same in both runs, except that the speed at which the live steam was blown through the tar was different. The results are shown in Tables I and II. The tables show that the speed has a slight effect on the concentration, that is, that a certain number of gallons of water in the form of steam going through the charge of tar will remove more acetic acid when the steam

TABLE I—SLOW SPEED

Time Start 12 : 50	Speed Gal. per Hr.	Total Distillate Gallons	Acid Per cent	In Fraction Pounds	Total Pounds	Pressure in Coils
1 : 05	40	10	20.6	17.1	17.1	45
2 : 05	30	40	19.35	48.1	65.2	43
3 : 05	25	65	13.31	27.6	92.8	46
4 : 05	24	89	9.68	19.2	112.0	41
5 : 05	23	112	6.25	12.0	124.0	43
6 : 05	26	138	4.62	10.0	134.0	43
7 : 05	24	162	3.00	5.9	139.9	35
8 : 05	23	185	2.12	4.1	144.0	42
8 : 35	22	196	2.08	1.8	145.8	40
9 : 05	22	207	1.87	1.6	147.4	40
9 : 35	24	219	1.69	1.6	149.0	41
10 : 05	12	225	1.61	0.8	149.8	45
10 : 35	12	231	1.52	0.8	150.6	45

Residual tar 0.28 per cent acid

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[1] There is no mysterious effect of "steam distillation" in this separation of acetic acid from tar. The steam is superheated all the time it is in contact with the tar and acts like any neutral gas in its effect on the distillation. In fact, as far as the *distillation* is concerned, the same fractionation of acid and oil would be obtained by direct fire heat in a distillation without steam The separation of acid from oil actually takes place after the condensation of the vapors when the acid is divided between the water and oil according to its relative solubility in these two substances. This indicates the desirability of washing certain fractions of the oil with water to recover a further quantity of acetic acid.

Table II—Fast Speed

Time Start	Speed Gal. per Hr.	Total Distillate Gallons	Acid Per cent	In Fraction Pounds	Total Pounds	Pressure in Coils
2 : 25	75	...	...	...	...	45
2 : 40	50	20	23.1	35.8	35.8	44
3 : 20	51	54	15.0	42.3	78.1	47
3 : 40	60	70	9.4	12.5	90.6	47
4 : 10	50	95	6.5	13.4	104.0	49
4 : 40	46	118	4.7	9.0	113.0	43
5 : 10	44	140	3.1	5.6	118.6	40
5 : 40	46	163	2.6	5.0	123.6	43
6 : 10	44	185	2.0	3.6	127.2	38
6 : 40	50	210	1.8	3.6	130.8	46
7 : 10	50	235	1.6	3.3	134.1	44
7 : 40	48	259	1.5	3.0	137.1	47
8 : 10	48	273	1.8	2.1	139.2	46
8 : 40	24	285	1.9	1.8	141.0	46
9 : 10	24	297	1.7	1.6	142.6	46

Residual tar 0.82 per cent acid

goes through slowly than when the steam goes through quickly.

A slow speed of distillation is, therefore, desirable from the standpoint of high concentration of distillate, and the speed should be kept as low as is consistent with the capacity of the tar stills. Sometimes it might even be desirable to build an additional still in order to make slower distillation possible.

EFFECT OF STEAM PRESSURE

The effect of different pressures of steam in the closed coils was not determined in the commercial still, but a laboratory experiment was carried out that showed this effect. Two charges of the same tar were distilled with steam. The tar was kept at a temperature corresponding in one case to a 10-lb. steam pressure, in the other case to a 50-lb. steam pressure. The results of the two distillations are shown in Table III.

Table III—Effect of Steam Pressure

	15 Lbs. Pressure				50 Lbs. Pressure			
Fraction No.	Cc.	Acid Per cent	Acid in Fraction Grams	Total Acid	Cc.	Acid Per cent	Acid in Fraction Grams	Total Acid
1......	66	3.5	2.3	2.3	58	6.8	3.9	3.9
2......	71	2.8	2.0	4.3	74	5.1	3.8	7.7
3......	78	2.0	1.6	5.9	69	2.5	1.7	9.4
4......	73	1.6	1.2	7.1	71	1.3	0.9	10.3
5......	77	1.1	0.8	7.9	73	0.45	0.3	10.6
6......	81	0.8	0.7	8.6	70	0.25	0.2	10.8

It is plainly to be seen from these results that more acetic acid can be obtained with less steam when the tar is kept at a higher temperature, that is, when the pressure in the closed coils is kept higher. For instance, at a 50-lb. pressure four fractions, with a total volume of 272 cc., contain 10.3 g. of acid, but, at a 15-lb. pressure six fractions, with a total volume of 446 cc., contain only 8.6 g. of acid.

END-POINT OF DISTILLATION

After it is known that a slow speed and high steam pressure are desirable conditions for tar distillation, to insure an efficient operation one other matter must be determined—the point at which to stop the operation. It may be seen from all three tables that the concentration of acid in the distillate decreases as the distillation progresses;[1] it finally reaches a point at which the concentration is so small that it is no longer profitable to recover acetic acid from the distillate. The proper degree of concentration at which to stop the distillation is determined, on the one hand, by the price of acetate, and, on the other, by the cost of the necessary fuel, labor, and apparatus. This computation must be made for each plant according to local costs for these items, the main cost being for the fuel required to make the steam for removing the acid from the tar and for evaporating the acetate of lime solution.

After the proper end-point for stopping the distillation has been decided upon, it is necessary to find a method for determining when this point has been reached. Probably most tar stills are operated on a time schedule. If the proper lengths of time are determined for reaching the end-point under certain constant conditions of distillation, and if those constant conditions could be maintained in subsequent runs, this method of operating the still would be satisfactory. However, variations in the original tar are unavoidable, and accurate regulation of speed and pressure are very difficult to maintain, so that the end-point cannot readily be ascertained by the length of time of distillation. The end-point is most accurately determined by an actual chemical analysis by titration of the acid contained in the distillate. This analysis may readily be made by the stillman if he is furnished with standard alkali and a graduated cylinder or pipette.

In some plants the dissolved tar left in the copper still after the distillation of the crude pyroligneous acid is mixed with the settled tar and distilled in the tar still; in other plants the copper still has sufficient capacity so that the dissolved tar may be distilled by steam without removal for the recovery of the acetic acid. In the latter case the same suggestions as to speed, pressure, and end-point apply to the dissolved tar in the copper still as to the settled tar in the tar still.

DIRECTIONS FOR TAR-STILL OPERATION

The following set of directions for running the tar still at one plant is given as an example:

(1) Distil with closed coils at steam pressure of 10 lbs. at the start, increasing to 50 lbs., as rapidly as possible without boiling over, until very little distillate is coming over.

(2) With steam in closed coils remaining at 50 lbs. or higher, if readily possible, blow in live steam at a speed of 30 to 35 gal. per hour when the charge is 40 in. deep (equivalent to 510 gal.), or at a correspondingly different speed when the charge is different. Continue this speed until 9.1 cc. of distillate are required to neutralize 10 cc. of 0.5 *N* alkali.

(3) Reduce the flow of live steam to at least one-half, and continue the distillation as long as not more than 9.4 cc. of distillate are required.

Such directions will, of course, vary with different plants and with varying conditions at the same plant. With the information offered in this paper, combined with a knowledge of local conditions, it should not be difficult to prepare a similar set of directions that would help to prevent loss of product on the one hand and loss of efficiency on the other.

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[1] There are two reasons for this: First, the proportion of acetic acid in the oil distilling over decreases as the distillation progresses, since the boiling point of the acid is lower than that of the oil; and second, the proportion of oil to water decreases, since at a constant temperature the vapor pressure of the residual tar decreases as the lower boiling oils are removed and more water vapor is required to carry over the same amount of oil.

THE HESS-IVES TINT-PHOTOMETER AND ITS USE WITH RAW SUGARS[1]

By George P. Meade and Joseph B. Harris

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The Hess-Ives tint-photometer is described by the makers as "an instrument for comparing different shades and hues of light colored materials or liquids with each other and with fixed standards, in order to differentiate and classify them and give them numerical expression." Light from an artificial daylight lamp placed at the back of the instrument shines on two blocks of magnesia from which it is reflected by means of a mirror through two adjustable light openings or slits into the instrument itself. The light from each slit is distributed over the corresponding half of a circular field by means of a patent device called an optical mixing wheel, which is rotated rapidly by a small motor. The left-hand slit may be adjusted from full open to tight closed by means of a shutter operated by a lever. The lever moves over a scale which reads zero when the slit is closed and 100 when it is open. The right-hand slit is adjustable through narrower limits, the adjustment being used to bring the two halves of the field to equal intensity when the lever actuating the left-hand slit is brought to 100 on the scale.

When a sample is placed on the magnesia block before the right-hand opening the light entering this aperture is reduced, and the corresponding half of the field appears darker. To measure the amount of the reduction the lever is moved down the scale until the field is matched again, and the amount the left-hand aperture has been closed is read on the scale. If the sample is of a gray shade without any specific color the field can be matched without the use of a color screen, but for colored materials readings are made by matching the field through each of the three color screens, red, green and blue-violet, provided with the instrument.

When working with liquids the solution to be examined is placed in a small glass cell with clear glass bottom on a shelf interposed between the right-hand magnesia block and the right-hand light opening, so that the light passes through the column of liquid. Provision is made so that no light enters the liquid except through the bottom. It is essential to place a cell containing distilled water to the same depth as the solution under examination on the shelf before the left-hand light opening, to compensate for the light cut off by the glass and the water of the solution. If this is done the same reading will be obtained irrespective of the depth of the column of liquid, provided the same amount of color is maintained. Our work has been done entirely with liquids, and no study has been made by us of the use of the instrument with solid materials.

The pamphlet accompanying the tintometer is vague, particularly as regards the arrangement of the attachment for liquids, and considerable study is necessary to set the instrument up properly. The position of the scale makes it awkward to read, but otherwise the tintometer as it comes from the manufacturers is well made and mechanically easy to operate.

SCALE READINGS

The problem which presents itself when the instrument is put into practical use is the meaning of the scale readings. The readings are in "per cent luminosity" or, subtractions of the readings from "one hundred per cent darkness." But how can these percentages be interpreted in terms of color concentration? Journal articles dealing with the tint-photometer which have come to our attention since this study was taken up also recognize this difficulty. Kress and McNaughton[1] add the three readings through the three color screens together and subtract from 300, calling the results "parts black." As will be seen later this method will serve only for readings in one part of the scale, and will then be only approximate.

Zerban[2] says, "since the readings obtained in degrees of the instrument bear no direct relation to the color concentration, it was first necessary to standardize the instrument for the purpose of translating the readings into concentrations." This he did by making an arbitrary standard solution of dark molasses, 30 g. per liter, and making up a series of dilutions containing 1 per cent, 2 per cent, 3 per cent, etc., up to 20 per cent, then by 2 per cent intervals up to 30 per cent, and by 5 per cent intervals to 100 per cent. Each of these solutions was then read in the tintometer through the three color screens and the readings recorded. He called the color of his standard molasses solution 100, and by comparing readings of other solutions with those obtained on the various concentrations of his standard he was able to express any scale reading in terms of the standard.

For reading solutions other than sugar solutions (*e. g.*, colorimetric determinations of iron and of the polyphenols) he made similar series of readings on standard solutions of the substance to be examined, but here he encountered the difficulty that "the color readings of the solution to be analyzed did not always agree in each color region with the readings obtained on those of known concentration."

INTERPRETATION OF SCALE READINGS

The tint-photometer was purchased by this laboratory for determining the color of raw sugars, and practically all of our study has been done on solutions of raw sugars. A weighed amount of sugar was dissolved in a given quantity of water, a liberal amount of kieselguhr added, filtered through paper, pouring back until the filtrate was brilliant.

A series of solutions of a certain raw sugar were made up containing, respectively, 1 g., 2 g., 3 g., in 25 cc. and readings were made on each of the solutions through each of the color screens. The tabulation shows the readings, which are presented graphically in Fig. 1.

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[1] Presented at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 15, 1920.

[1] "A Numerical Expression for Color as Given by the Ives Tint-Photometer," This Journal, **8** (1916), 711.

[2] "The Color of Sugar Cane Products," *Louisiana Bulletin* **165**, March 1919.

The instrument is accurate to one degree of the scale, the blue field being somewhat more difficult to match than the others.

Table I—Readings on Various Strength Solutions of the Same Raw Sugar, Showing the Variation of the Scale Readings for Concentration

Sugar in 25 cc. G	Red Screen	Green Screen	Blue Screen
1	87	74	47
2	75	55	24
3	65	40	12
4	57	30	7
5	50	22	Too
6	43	16	dark
7	37	12	to
8	32	8	read
9	27	6	accu-
10	24	4	rately

It is seen from these figures that neither the scale readings themselves nor the scale readings subtracted from 100 are direct expressions of the relative amounts of color, but that as the amount of sugar is increased the scale readings decrease by a constantly decreasing amount.

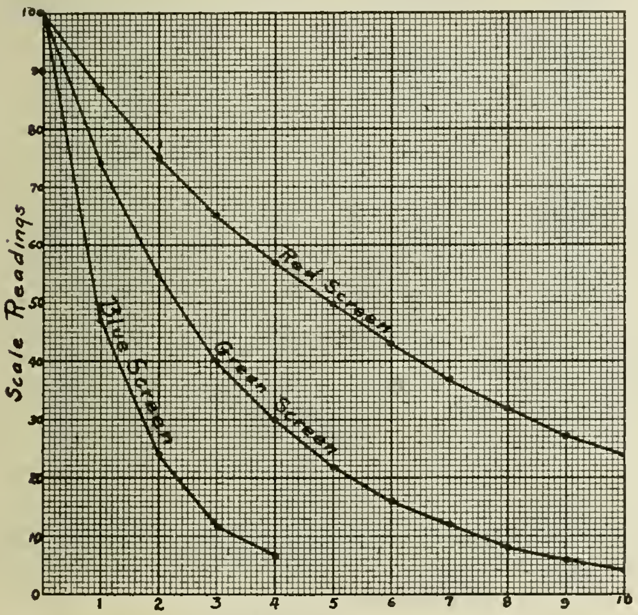

Fig. 1

A study of these curves and figures and of other similar series brought out the fact that the readings in any series run in powers of the first reading of the series, *i. e.*, the reading for one unit of material, no matter which color screen or what class of material was used. (For mathematical purposes, the scale readings must be considered as decimal fractions.) For example in the first series given in Table I: $.87 \times .87 = .757 \times .87 = .658 \times .87 = .574$, etc. The scale does not admit of the reading of fractions.

The reason why the readings follow this rule lies in the make-up of the instrument itself. Consider the two halves of the field evenly matched with the scale set at 100, *i. e.*, with the same amount of light entering both apertures. Now if a solution containing one gram of the sugar used in Table I is placed before the right-hand opening, it will permit only 74 per cent of the light to pass when viewed through the green screen. To match the field again, the left-hand opening must be reduced until it is 74 per cent of its size, or, in other words, the lever must be moved down the scale to 74. The conditions are now the same as when the instrument was in adjustment at 100; the same amount of light is entering both apertures and the field is evenly matched.

The first solution is now replaced by one containing 2 g. of the sugar. This second gram of sugar will cut off the same *percentage* of light that the first gram did, that is, it will permit only 74 per cent of the light now entering to pass, and the left-hand opening must be closed to 74 per cent of its present width in order to match the field again. ($.74 \times .74 = .548$ or 55 in practice.) A third gram of sugar will again reduce the light 74 per cent of the amount entering after the field is matched with the 2 g., and the scale must be moved to 74 per cent of .548, or .406, a reading of 40 in practice.

This relationship between the scale readings and the amount of material taken can be expressed algebraically by the equation $y = K^x$,

where y = any scale reading
K = the scale reading for one unit of the material
x = the number of units of material which will give the scale reading y.

With this equation, given the scale reading for a unit amount of material, it is possible to calculate what reading would be obtained with any other amount of the same material; or, given the scale readings of unit quantities of two materials, the amount of color in the one as compared to the other may be computed.

For example: To find what 5 g. of sugar would read through the red screen, given that one gram reads 87,

$$y = .87^5 = .498 \text{ or } 49.8 \text{ against } 50 \text{ in practice (Table I)}$$

Five grams of Raw Sugar A read 58 through the green screen; the same quantity of Raw Sugar B reads 41. Problem: To find how much more color B has than A or how much of A would be required to give the reading of 5 g. of B.

Solving the equation for x:

$$x = \frac{\log\ y}{\log K} = \frac{\log .41}{\log .58} = \frac{.3873}{.2366} = 1.636$$

That is, through the green screen, B has 1.636 times as much color as A, or it would require 1.636 times as much of A to give the reading of any given quantity of B.

To prove this in practice, a solution containing 8.2 g. of A (1.64×5 g.) was read through the green screen. One observer read 41, the other 42, as against a reading of 41 for 5 g. of B

Through the red screen, 5 g. of A read 78, and 8.2 g. read 67. What should the 8.2 g. have read according to the equation?

$$y = .78^{1.64} = .665 \text{ or } 66.5 \text{ on the scale}$$

TABLE FOR TRANSLATING SCALE READINGS TO UNITS OF COLOR

It is also possible by means of the equation to compare all scale readings with some fixed number as a standard. This has the advantage that K becomes a constant in the logarithmic calculation.

To avoid repeating the logarithmic calculation, we adopted K = 99 as a standard, and calculated a table by means of the equation for each scale reading from 100 to 1 (Table II). By this table all solutions are compared to a hypothetical solution which would give a reading of 99 for all three color screens. The number 99 was selected because it represents the smallest amount of color which can be read in the instrument, and therefore the color corresponding thereto can be taken as unity. The table gives opposite each scale reading (y) the number of units (x) of the hypothetical solution (K = 99) which it would take to give the scale reading; or, taking the color of the hypothetical solution as unity, the number of color units corresponding to that scale reading.

TABLE II—FOR TRANSLATING HESS-IVES TINT-PHOTOMETER SCALE READINGS TO UNITS OF COLOR

$y = K^x$, where y = scale reading; x = units of color; K = 99 (constant)

Scale Reading y	Units of Color x	Scale Reading y	Units of Color x	Scale Reading y	Units of Color x	Scale Reading y	Units of Color x	Scale Reading y	Units of Color x
100	0.0	80	22.2	60	50.8	40	91.1	20	160.0
99	1.0	79	23.4	59	52.5	39	93.6	19	165.0
98	2.0	78	24.7	58	54.2	38	96.2	18	170.5
97	3.0	77	26.0	57	55.9	37	98.9	17	176.0
96	4.0	76	27.3	56	57.7	36	101.6	16	182.0
95	5.1	75	28.6	55	59.4	35	104.4	15	189.0
94	6.1	74	29.9	54	61.3	34	107.3	14	196.0
93	7.2	73	31.2	53	63.1	33	110.3	13	203.0
92	8.3	72	32.6	52	65.0	32	113.3	12	211.0
91	9.4	71	34.0	51	67.0	31	116.5	11	219.0
90	10.5	70	35.5	50	68.9	30	119.7	10	229.0
89	11.6	69	37.0	49	70.9	29	123.1	9	239.5
88	12.7	68	38.4	48	73.0	28	126.6	8	251.0
87	13.8	67	39.9	47	75.1	27	130.2	7	264.0
86	15.0	66	41.3	46	77.2	26	134.0	6	280.0
85	16.2	65	42.8	45	79.4	25	137.8	5	298.0
84	17.4	64	44.4	44	81.6	24	141.9	4	320.0
83	18.6	63	46.0	43	83.9	23	146.2	3	349.0
82	19.8	62	47.6	42	86.2	22	150.6	2	389.0
81	21.0	61	49.2	41	88.7	21	155.0	1	458.0

Any of the illustrations used to show the workings of the equation can now be worked out much more simply by the table.

For example: To find what 5 g. of sugar would read through the red screen, given that 1 g. reads 87.

From the table, 87 = 13.8 color units

$$13.8 \times 5 = 69.0$$

From the table, 69 corresponds to a scale reading of 49.8 (50)

Sugar A reads 58 through the green screen

Sugar B reads 41 through the green screen

From the table, 58 = 54.2 color units; 41 = 88.7 color units

Then B has $\frac{88.7}{54.2} = 1.64$ times as much color as A

By means of the table, then, any scale reading for any color screen can be immediately translated into units of color, irrespective of the class of material under examination.

DETERMINATION OF COLOR OF RAW SUGARS

The following method for determining the color in raw sugars has been adopted: Dissolve 20 g. of sugar in distilled water and make up to 100 cc. Filter through paper in which are placed two or three teaspoonsful of kieselguhr, pouring back until the filtrate is brilliant.

Transfer 25 cc. of this solution to the observation cell on the right side of the instrument, and place a cell containing 25 cc. of distilled water on the left-hand side. Read the solution through each of the three screens, record the readings, and note the color units for these readings as taken from the table. Add the color units thus obtained and divide by three, recording this as the color of the sugar. Whole numbers only are used.

In case the sugar is so dark that any of the readings fall below 20 it is best to take a smaller amount of the solution (diluting it to 25 cc. if desired). The result can be calculated to 5 g. The instrument is rather hard to read accurately in the lower part of the scale, and one degree error with the lower numbers of the scale represents a much greater amount of color than with the higher scale readings.

The use of 5 g. and the division of the sum of the color units by three were adopted as they were found to give convenient sized numbers for our work. The time required to make a color determination in this way is about the same as that required for a direct polarization.

TABLE III—TYPICAL RESULTS OF COLOR DETERMINATIONS ON RAW SUGARS

Class of Sugar	Scale Readings Red Screen	Scale Readings Green Screen	Scale Readings Blue Screen	Units from Table Red Screen	Units from Table Green Screen	Units from Table Blue Screen	$\frac{\text{Total Units}}{3}$ or Color
Cuban Raws 1920 Crop......	64	40	12	44.4	91.1	211.0	116
	65	41	16	42.8	88.7	182.0	105
	66	47	25	41.3	75.1	137.8	95
	70	50	21	35.5	68.9	155.0	87
	72	52	25	32.6	65.0	137.8	78
	71	53	31	34.0	63.1	116.5	71
	70	55	37	35.5	59.4	98.9	64
	80	62	35	22.2	47.6	104.4	58
Cuban Raws 1919 Crop......	59	29	10	52.5	123.0	229.0	135
	69	42	16	37.0	86.0	182.0	102
	72	53	41	32.6	63.1	88.7	62
Washed Raw 1919 Crop......	84	76	53	17.4	27.3	63.1	36
1920 Crop......	99	97	85	1.0	3.0	16.2	7
Refinery High Remelt...	95	89	73	5.1	11.6	31.2	16
Refinery Molasses Sugar One Gram....	73	51	23	31.2	63.1	150.6	82

(Calculated to 5 g.) 82 × 5 = 410

SUMMARY

The scale readings of the Hess-Ives tint-photometer are meaningless in themselves as they do not express directly the relative amounts of color.

It was found that the scale readings for solutions containing 1, 2, 3, 4, etc., units of material run in powers of the reading for one unit, considering the scale readings as decimal fractions. This is due to the mechanical make-up of the instrument, and is true no matter which color screen or what class of material is used.

Expressed algebraically, this relationship between the scale readings and the amounts of color becomes $y = K^x$, where y is any scale reading, K is the reading for one unit of material, and x is the number of units of material required to give the scale reading y.

By means of this equation solved for x the color of two materials may be compared, given scale readings for equal quantities; or all scale readings may be compared to a standard.

To avoid the repeated calculation, a table has been calculated which gives the units of color corresponding to each scale reading from 100 to 1. A convenient method for determining the color of raw sugars, using the table, is given, together with results for various sugars.

PRESERVATIVES FOR FERMENTABLE BEVERAGE SAMPLES

By J. S. McCune and A. N. Thurston

Division of Laboratories, Ohio State Department of Health, Columbus, Ohio

Received October 27, 1919

Before prohibition went into effect, the Liquor Licensing Board in Ohio was collecting many samples of alcoholic beverages in connection with the licensing laws. These were analyzed at the Department of Health Laboratory, where all state analytical work is now done. Some of the samples collected in territory which was dry because of local option were near beers and ciders.

Argument arose about these samples as to the possibility of fermentation before delivery to the laboratory, but after the sale of the liquid. With near beers and particularly with ciders there was no doubt as to this having occurred in some instances where delivery was unavoidably delayed. For the purpose of testing out the necessity of preservatives, and the chemicals best suited for this use, coöperation between the two departments was arranged. However, when prohibition became effective, the Liquor Licensing Board ceased to exist, which has handicapped the work to some extent. Sweet cider could not be obtained, and so the preliminary experiments have been made on near beer. The tests are of interest, however, and will be of value in court cases for the enforcement of dry laws in the state.

The experiments made are listed below, and since lack of samples has prevented any extensive study, the conclusions are open to revision. Information from any bureaus or departments engaged in control work would be welcome.

EXPERIMENT 1—"Bruin," a near beer manufactured in Columbus, Ohio, and sold in bottles, was allowed to stand open at room temperature.

Alcohol Content: Per cent by Volume

Original	None
After 1 day	None
After 2 days	None
After 5 days	0.19 (heavy mold growth)

Conclusion: The bottled beer would not ordinarily ferment, even when open.

EXPERIMENT 2—Same, with 1 cc. of a suspension of Fleischman's yeast.

Alcohol Content: Per cent by Volume

Original	None
After 1 day	1.47
After 5 days	2.05

Conclusion: With yeast 2.00 per cent alcohol were obtained, the large portion in 24 hrs.

EXPERIMENT 3—Bruin and 1 cc. yeast as above, but with varying preservatives, each added as 0.20 per cent.

Alcohol Content: Per cent by Volume

	Mercuric Chloride	Salicylic Acid
After 1 day	0.20	0.20
After 4 days	0.13	0.10
	Sodium Benzoate	Sodium Bisulfite
After 1 day	0.16	0.73
After 4 days	0.10	2.20

Conclusion: Two-tenths per cent of mercuric chloride, salicylic acid, or sodium benzoate are satisfactory to prevent fermentation. The same percentage of sodium bisulfite is unsatisfactory.

EXPERIMENT 4—Same as Expt. 3, but beer was allowed to ferment one day before adding preservative, to determine whether started fermentation would be checked.

Alcohol Content: Per cent by Volume

	Mercuric Chloride	Salicylic Acid
After 1 day, without preservative	1.08	1.04
Same, 3 days, after preservative added	1.04	1.02
	Sodium Benzoate	Sodium Bisulfie
After 1 day, without preservative	1.04	1.04
Same, 3 days, after preservative added	1.95	1.89

Conclusion: Two-tenths per cent of mercuric chloride or of salicylic acid are satisfactory to check started fermentation, but the same amount of sodium benzoate or sodium bisulfite is unsatisfactory.

EXPERIMENT 5—Same as Expt. 4, but with sodium benzoate only, to determine whether the sodium benzoate result could be confirmed.

Alcohol Content: Per cent by Volume

	Sodium Benzoate No. 1	Sodium Benzoate No. 2
One day's fermentation before adding benzoate	0.47	0.48
After 3 days additional with 0.20 per cent benzoate	1.94	1.95

Conclusion: Sodium benzoate (0.20 per cent) is unsatisfactory to check fermentation.

EXPERIMENT 6—Draft near beer, purchased from keg, with 0.20 per cent sodium benzoate and without, to determine whether draft beer would ferment without added yeast and whether benzoate would prevent the fermentation.

Alcohol Content: Per cent by Volume

	Without Preservative	With 0.20 Per cent Benzoate
As purchased	0.43	0.43
After 1 day	1.18	0.47
After 3 days	1.43	0.43
After 8 days	..	0.43 (heavy mold growth)

Conclusion: (*a*) Draft near beer would ferment rapidly as purchased; (*b*) sodium benzoate, 0.20 per cent, prevented this fermentation.

EXPERIMENT 7—Draft near beer, without yeast, preservatives, 0.20 per cent, added on day of purchase.

Alcohol Content: Per cent by Volume

	Mercuric Chloride	Salicylic Acid
As purchased	0.63	0.63
After 3 days with preservative	0.63	0.60
	Sodium Benzoate	Boric Acid
As purchased	0.63	0.63
After 3 days with preservative	0.75	1.53

Conclusion: Mercuric chloride, or salicylic acid (0.20 per cent), satisfactory to prevent fermentation; sodium benzoate (0.20 per cent), doubtful; boric acid (0.20 per cent), unsatisfactory.

EXPERIMENT 8—Draft near beer as in Expt. 7, but preservatives added after one day's standing.

Alcohol Content: Per cent by Volume

	Mercuric Chloride	Salicylic Acid
As purchased	0.63	0.63
After 1 day without preservative	1.35	1.35
After 3 days additional with preservative	1.30	1.36
	Sodium Benzoate	Boric Acid
As purchased	0.63	0.63
After 1 day without preservative	1.35	1.35
After 3 days additional with preservative	1.50	1.56

Conclusion: Fermentation nearly complete in one day, but results in general checked conclusions of Expt. 7.

GENERAL CONCLUSIONS

These experiments show the efficiency of the above preservatives used in untreated draft beer and bottled beer treated with Fleischman's yeast.

Sodium benzoate, 0.20 per cent, is unreliable as a preservative.

Sodium bisulfite and boric acid, 0.20 per cent, are worthless.

Mercuric chloride and salicylic acid, 0.20 per cent, are satisfactory preservatives.

Due to the poisonous nature and higher cost of mercuric chloride, salicylic acid, 0.20 per cent, is recommended as the preservative to be used when fermentable samples are to be tested for alcohol content and when immediate delivery to the laboratory is not possible.

A SIMPLE ALCOHOL-TESTING DEVICE[1]

By Sigmund Waldbott

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Received December 16, 1919

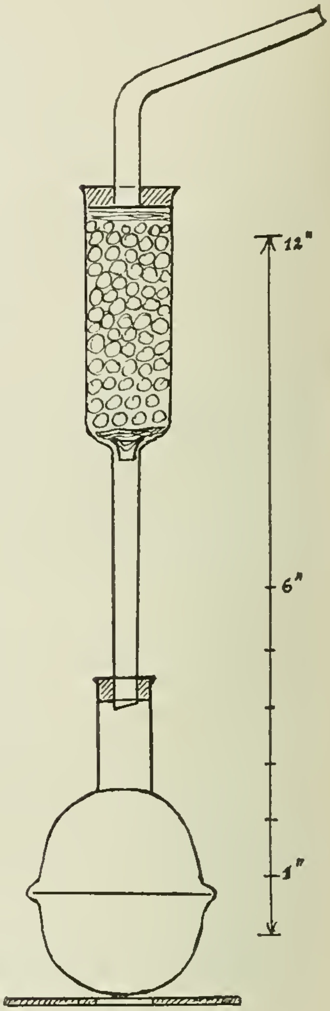
A simple device has been developed which readily differentiates between a beverage of low alcohol content, *e. g.*, 0.5 per cent, and one containing more, *e. g.*, 3 per cent alcohol. It is not intended to replace the exact methods of alcohol determination, but rather to aid them, by giving preliminary information as to alcoholic contents. Its principle is to boil out the alcohol, separate it from the water vapor by means of a simple fractionating device, and demonstrate the alcohol vapor by ignition.

The apparatus consists of a copper flask and a fractionating attachment as shown in the sketch, made of glass or metal. The fractionating medium consists of glass beads which fill the receptacle of the attachment. The bend in the exit tube has some advantage in the demonstration. In heating the flask by a Bunsen burner, or by an alcohol lamp, use an asbestos plate with a 1-in. opening in the center.

Fifty cc. of the fluid, *e. g.*, beer, are put into the flask, and heated over a medium-sized Bunsen flame to boiling, regulating the flame according to apparent needs. When using a glass attachment, the progress of condensation is easily observed. In the case of metal, the sense of touch will tell. When the alcohol vapor appears at the orifice, ignite it with a burning match or candle.

If the beer contains 3 per cent alcohol, a semi-luminous, blue flame about 3 in. long will continue to burn for 120 to 150 sec. depending on the size of the Bunsen flame. When the beer contains only 0.5 per cent alcohol, the flame of the same length lasts about 20 to 25 sec. under the same conditions of heating the bulb. Thus the duration of the flame is approximately proportional to the alcohol contents. To this extent, the apparatus permits even approximate quantitative estimations.

The apparatus may serve as a lecture experiment, and may prove useful as a legal instrument in the hands of government officials charged with the enforcement of laws relating to alcoholic contents of beverages.



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[1] Presented at a meeting of the Cincinnati Section, American Chemical Society, October 15, 1919.

ADDRESSES AND CONTRIBUTED ARTICLES

A PLAN FOR INCENTIVE TO RESEARCH IN PURE AND APPLIED CHEMISTRY[1]

By William J. Hale

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In these post-bellum days of industrial reconstruction we cannot fail to note the prominence gained by American chemists. Those with adequate training and experience meet with little difficulty in their forward progress, but far too many realize more and more that lack of broader training in their early academic career. Only those young men thoroughly grounded in the fundamentals of their science and well versed in engineering and mathematics can ever expect to gain the prominence they seek. Colleges everywhere must recognize this situation and strengthen decidedly their prescribed chemical training.

For the university man who is soon to enter actively the chemical profession it has thus appeared as most reasonable to recommend the further pursuit of the science for a year or more on some problem of research, and under competent guidance; to this end a number of industries have endeavored to lend encouragement through the offer of material aid. This aid usually follows some plan more or less in keeping with precedent at the particular university and beyond this much is left to the good will of all concerned. Though the best of motives may have prompted this action on the part of the industries, I feel that they have not sufficiently weighed the outcome of their well-intended efforts. In other words, I believe that a far better plan for the furtherance of chemical research lies open to us. You may characterize my plan as daring, but I shall choose to call it the plan of incentive, and in order to draw support for my propositions, I wish now to analyze the present-day conditions.

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[1] Read at the 59th Meeting of the American Chemical Society, Division of Industrial and Engineering Chemistry, St. Louis, Mo., April 12 to 16, 1920. A committee has been appointed by this Division to study the questions berein presented and to draw up a definite plan for actiod.

Introductorily speaking, I found myself only a few years ago firm in the conviction, unreasonable to the point of intolerance, that any research save that in pure science was merely guesswork. Its degrading effect was apparent to all who really studied the question and hence I constituted myself a disciple of pure unadulterated chemistry. Do not think me alone in this category. Too many, yes, far too many of our chemists thought alike with me. We all entertained a horror of perverting the science to mundane ends, and thus, in contrary fashion, sought steadfastly to elevate it at least into terrestrial temples. The march of progress has made steady inroads upon chemical knowledge; the simpler points readily yielding to industrial development, as noted so well by the applications of inorganic and physical chemistry. Applications of the more complex, the physiological and organic, have only recently come into prominence. In this latter field I am obliged to characterize myself as having held aloof and thus ensconced its isolation from a world of activities. Whether or not I have erred I leave to you to judge.

TYPES OF RESEARCH

Let us consider briefly three general types of research in operation. First, the purely industrial research carried on in industrial laboratories either in connection with specific industries or under independent organization. Second, university research which, as its name implies, embraces those researches conducted at a university either by the university staff or its advanced students. And third, the endowed research or that type supported by permanent endowments and placed under the direction of our institutes of research.

This latter class is indeed ideal in its organization and deserves our heartiest support. The highest class of work may here be accomplished through the employment of well-known scientists. It is possible also that a number of these purely research men may be attracted by universities to research professorships, the highest possible bestowal of honor by any university, and there exert a marked influence upon scientists yet in the making. An admirable outline of this plan with its purpose and scope is to be found in an address by Dr. R. A. Millikan, entitled "The New Opportunity in Science," and published in *Science*, September 26, 1919. In one sentence, "Our greatest need is not for facilities, but for the selection and development of men of outstanding ability in science," Dr. Millikan has summed up the situation of scientific endeavor in America, and upon this theme rests the *raison d'être* of my discussion.

The first or purely industrial type of research will receive due consideration throughout my discussion. It must be recognized as broad in scope and broadening more day by day. The results, however, for commercial reasons do not find immediate publicity save in patent literature, and this literature, I regret to state, is little fathomed by American chemists. It is coming rapidly into prominence and bids fair to rank as high here as it does in other countries. In many cases, the applications for a patent far outrank some of the most noted articles appearing in our purely scientific journals.

It is the second or university type of research that I would now set before you for analysis. It will be necessary for us to consider it in detail and for this purpose I choose to mention the two distinct policies in its prosecution. The first policy comprehends the operation of those special departments, usually at state universities, where competent men are employed to investigate questions affecting the health and welfare of the public. The men thus engaged are subject to call for assistance on the part of various public organizations, but they are able also to devote considerable time to problems of research, and much good results therefrom. As an outgrowth of this plan we may view the possible establishment, already under discussion at several universities, of Research Bureaus, at the request of various manufacturers' associations. These bureaus are to be organized to handle problems submitted to them by the manufacturers. The reports no doubt are to be made public, but at the same time to be utilized by whatsoever manufacturer directly interested. Though good results may be attained, the researches themselves will rarely embrace any more than passing fancies. In this day any vital question necessary for a growing manufacturing establishment will have its best investigators closely connected with the establishment—otherwise the manufacturers might well seek some more elementary pursuit. The scheme, however, should work to advantage in promulgating new enterprises and offering new possibilities to old ones. Further, it will acquaint the university man with elementary industrial problems and thus serve to widen his all-too-narrow vision to the point of making him more decidedly human—an attribute most desirable in those who would teach others.

The second policy comprehends the operation of the graduate schools and corresponding faculties in research for itself alone. Students enrolled in these graduate schools receive a thorough training as ground work for their chosen subject and find it possible to devote about half of their time to special research. Within a few years they are enabled thus to attain the degree of Doctor of Philosophy, and the results of these researches immediately find publicity in our scientific publications. It is this form of research that appeals strongly to those who have received just such training. Naturally it may be contended that this is only the early stage in research work. True, of course, but much of value I believe may be accomplished by the student in this prescribed course, especially so if he is of mature and original mind.

In order that students may be encouraged to spend these few extra years at the university, various kinds of assistantships and fellowships are open to award. The assistantships offer only small recompense but are of inestimable value where not more than a quarter of the students' available time is required. The fellowships carry with them a not inconsiderable stipend or honorarium without the adjunct of teaching responsibilities and when awarded upon the basis of merit and ability alone there is no higher honor in student life. Both assistantships and fellowships, therefore, concern us directly as research opportunities.

INDUSTRIAL FELLOWSHIPS

I come now to the particular point at issue. In recent years we note the introduction of a new class of fellowship—possibly falling under the supervision of graduate schools but more or less removed from such beneficent influence and left to various departments as distinctly technical and pertaining more directly to a super-graduate school; at least the holder of such fellowship will preferably be chosen from among those who have attained their doctorates. I refer to the so-called industrial fellowship established by such and such company at this or that university—a living stipend for the Fellow, reservation of publications by the university, but nevertheless certain prior claims in honor due as reports to the company. Though a number of such fellowships have been maintained throughout American universities in former days, this number has been more than trebled during the past year or two; a direct result of the war, as you may infer, and yet more directly a result of growth and advertising on the part of the specific industry. At bottom, however, the industries will eventually benefit by the further training of our young chemists, and if industral fellowships alone were to make this possible, then industrial fellowships there must be.

It is my purpose to criticize this purely industrial fellowship and offer a new plan which I believe will accomplish all that the founders of fellowships could ever hope for and at the same time give to each and every chemist, no matter where or how situated, an equal chance with every other chemist to do and to make or the betterment of himself and his profession. Possibly I fought first to characterize what I shall call the scientific stupidity of any, if such there are, who believe that a young chemist, as holder of a fellowship, is suddenly endowed with such powers as will enable him to assist any particular industry in solving some all-important problem. Were the holder of a fellowship of equal rank to a Doctor of Philosophy, as the average instructor, I still could not be persuaded that he had anything at all in his favor unless perchance he had first-hand and direct knowledge of the industrial side of the question before him. If, on the other hand, the fellowship is awarded to a mere graduate in chemistry or chemical engineering, he has no chance whatsoever of accomplishing anything worth while in shorter time than a less well-trained chemist could accomplish under proper guidance at the chemical plant itself.

TECHNICAL AND PHILOSOPHIC PROFESSORS

This is not an arraignment of our college graduates in chemistry. Latently they possess much ability and knowledge and will develop in good order when once introduced to chemical practice. They display, however, little evidence of chemical common sense; their minds function but not in unison with the reactions before them. Only practical experience with abundant responsibility will develop them effectively for serious work. This same adverse criticism is not alone applicable to the young chemist graduate. It is even more applicable to the average professor. Certain professors, the technical professors, who are indeed scientific artisans, have become well informed in matters of chemical industry and realize the importance of industrial procedure over recognized methods. The artless, however, the philosophic professor, is that class of man who never pictures to himself the conditions necessary for worldly success. It is extraneous in his make-up. To him processes in plant operation are merely large-scale laboratory experiments. I have yet to learn of a process developed in the laboratory which remained identical with its original set-up when once the process had been placed in operation in a plant. There may be one on record, but none has been reported to me from numerous inquiries of industrial leaders. How less likely then are the students of these philosophic professors ever to be able to cope with industrial problems. The technical professor naturally will be abundantly able to direct the students in proper style if he himself continues to keep abreast of the times, but this type of professor is so rare that we can hardly expect the result of his teaching to produce more than a ripple on the sea of chemical training for yet a few years. It is not my intention to belittle the work of the philosophic professor. I intend to show that it should be ideal. He ought not, however, to concern himself with industrial research. It is beyond his ken. How few, however, of these very philosophic professors will thank me for my words. They know; they comprehend; their vision is full; all is as glass. Bear with me in this invective, for remember I was once as such. It is this type of man one enjoys showing about a chemical plant. They converse learnedly, admire swiftly, condemn idiotically, and depart thinking they have learned something of the various steps in our processes. The technicist arrives and is aware of his ignorance. He departs and realizes he has yet much to learn. He is the kind though who knows that it is absolutely impossible for the greatest chemist on earth to learn much at a plant beyond what is scheduled for him to learn. There are some reported as still extant who think they can learn by observation alone.

ANALYSIS OF PRESENT STATUS OF CHEMISTRY IN AMERICA

As my theme concerns itself with the development of men into able chemists, it is manifest that this second type of university research policy—the graduate school—affords the greatest opportunity for broad and higher training and hence for betterment of chemistry in America. I shall confine myself therefore to this phase of the subject, and aim to show the actual interdependence of research in both scholastic and applied domains. In order that I may draw support for my constructive plan of research, I wish first to typify the present status of chemistry in America as visualized in both university and industry. I make bold, therefore, to introduce four premises and after their cursory examination we shall pass directly to my conclusions. Inwardly I delight in such procedure, for by these very premises I wish, as it were, to offer my critics their choice of weapons.

My first premise, as follows, will probably incite greatest furore: *There is scarcely any possibility of direct advance in industrial chemical enterprise through industrial research undertaken in a chemical laboratory of a university.* Five years ago there was every possibility of such an advance. Since then the transition is complete and the suddenness of it simply baffles our imagination. During this period of transition a number of men actually developed processes which stood ready for semi-plant operation. This eventuality may occur again sporadically but it will more than likely be the result of some enthusiast coming upon new ideas which he is particularly well suited to develop alone. The enormous strides recently made by the industries have reacted in fact upon these organizations and they have come into a full realization of the importance of constant and continuous research as a *sine qua non* for healthy and vigorous growth. The industrial laboratories are equipped for every phase of work attending their plant processes, and are fast approaching the most ideal conditions necessary for those new features which stand in contemplation. Every modern appliance is placed at the chemist's disposal; whatever he desires he has but to mention and the most costly contrivance is provided without a moment's hesitation. The thought of farming out, as it were, any new project of an industrial plant to a university laboratory is ridiculous in the extreme and the horrible thought of asking some outside party to conduct researches, to assist the plant with difficulties underlying any one of its valued processes, is utter nonsense—almost sacrilegious. The only possibility thus left to an outsider will be the investigation of minor points which in themselves are valueless but which, through more detailed and extended study, may appear in new garb and become of value when they again are turned over to the industrial specialists. A little outside investigation at little cost may save time and energy on the part of the really productive men; quite so, but I must soon demonstrate the criminal nature of this procedure.

Granted, however, that industrial fellowships are to be founded only for altruistic purposes and that they are to carry with them no ties whatsoever to influence the recipient to take up industrial problems, there remain yet two most necessary adjuncts—the fellowships must be awarded through some manner of examination and the holder must be subject to the rulings of the graduate schools. I do not hesitate to recommend a Board of Examiners who shall prepare questions and submit the same to possible candidates at certain stipulated times and places. The successful candidates will then select the university and type of work they hope to pursue. Any method of establishing such ideal industrial fellowships at this or that university because of some family ties or of some favored influence is not to be encouraged in this modern era. What chemistry needs is able men, what able men need are energy and enthusiasm. These cannot come into being through continuation of old, befogged ideas. The young men must seek out the real enthusiasts in the chemical world and together they will make for advancement. Thus, I believe, the young fellowship men should be given *carte blanche* to go to whatsoever university they would and seek the guidance of those men most highly esteemed in the scientific world. University instructors everywhere soon would picture to themselves that goal of goals: wherein they, through the publication of excellent researches, might be able to draw brilliant young chemists to their laboratories. With industrial fellowships thus constituted as a type of higher university fellowship I doubt if any can deny the highly beneficial effect this plan may exert, but this particular ideal industrial fellowship I have outlined does not seem to be the type recently launched. Indeed that form most frequently brought to our attention is an industrial fellowship founded for industrial ends, and, if perchance the industrial purpose is dormant, the fellowship is apparently allotted to a university with power to act. The baneful effect of this latter step may be gathered from my earlier remarks.

THE UNIVERSITY EVIL

In further corroboration of my first premise and distinctly as basis of my second, I must express myself on the evils that obtain at our universities and are operating in such manner as to retard the very advancement of chemistry in America. Do not think for a moment that I wish to enumerate all of the defects that may be apparent either here or there in the university world, but let me state my second premise gathered from many observers and fast becoming known to all: *The science of chemistry in the American university to-day is not keeping pace with its advancement in the industries.* Many of my hearers will scorn this remark, many will question my veracity, but none can disprove it. Of course, there are some outstanding advances in the realms of the pure science itself, but for every one of these I can cite two or three remarkable discoveries made outside the academic walls. That I may escape the brunt of possible criticism, allow me to read at once a recent statement by John Hayes Hammond: "Our universities do not lead in scientific thought, but usually follow. In mining, in engineering, and in nearly all of the professions excepting possibly medicine, where the union between teaching and practice is admirable, the universities are as a rule well behind instead of well ahead of current practice. It cannot be otherwise if the teaching staffs are in touch with current practice only by hearsay."[1]

This statement I assure you will be substantiated by the great majority of America's best chemists. But the cause is what I seek, and herein lies a university evil that escapes our earnest efforts to combat. This evil is briefly expressed. The university authorities do not recognize the absolute subservience of ability to enthusiasm and energy on the part of their teaching staff. The industries employ chemists of just as much and even more ability than the universities, but the industries prize those men who possess greatest energy and enthusiasm. These are the men who master almost superhuman difficulties and accomplish ends almost unbelievable. I will grant that this same type of men would play havoc within moss-covered walls. My critics, of course, will insist that my reference must chiefly concern mechanical questions, but can you cite for me any chemical process that is not in the main mechanical? I can reverse hundreds of processes which run apparently in one way in your laboratory because of your peculiarly small volume reactions within narrow ranges of temperature, pressure, and catalyst. The man who has taught chemistry for a long time and accustomed himself to think in certain time-worn channels and to operate in certain erroneous textbook methods of procedure is almost useless in a plant. His advice as to how the industries should handle questions is worse than useless. All respect him but his day is done.

DEGRADATION OF UNIVERSITY INSTRUCTOR

There is, however, at the university a type of man whose interests I have at heart. This is the young instructor, the newly fledged Doctor, but a man who has in him all that American chemistry needs for the future. He has ability, of course, and his energy and enthusiasm are growing in leaps and bounds. His reputation is all before him, but he is unfortunately human. The salary he earns is meager and it really cannot be otherwise, for you would not advise a sumptuous salary till he has shown his worth. Above all, he has highest hopes of achieving something and thus he should be given all the aid possible. Amid the difficulties that encompass this young instructor, the lack of competent student assistants to aid his researches, and the continual encroachments on his free time weigh more and more heavily. His advancement is found to depend upon so many factors that he soon comes to realize that the least important is his productivity in research; the most important, unfortunately, is his subservience to those higher up. It may be that the young man will seek to gain recognition through general service in university activities, or he will seek outside work more often in the capacity of analyst for industrial corporations. In both events his ability to accomplish the bigger things in chemistry is likely to atrophy and that is the end of him. What the young chemist needs is actual help and guidance on the part of the older men, and all the assistance possible heaped upon him. Encouragement possibly, in a word, will express my meaning, if the financial side is not overlooked, and where there is a likelihood of university trivialities making an inroad upon his time, the older men should guard him against the evil thereof. The young man's energy and enthusiasm is bound to carry him forward, but unless he is guarded on every hand his ability in the service of chemistry will soon be lost sight of amid the daily routine roundabout. Think of the constant interruption at a university in one's plans for investigation. Think of the childish meetings for discussions which may be far better handled, classified, and solved by an average clerk. Will the universities ever wake up to the importance of advancement in their several sciences and humanities to the utter banishment to Augean stables of all the silly nonsense that encumbers the many departments? Why permit this perversion of enthusiastic young chemists, with marked ability to accomplish something worth while, to the role of clerk and committee-man just because he has energy and a goodly nature withal. So soon as a university chemist is drawn into clerical work and begins his lifelong service on a committee for this or a committee for that, that moment his future possibilities in advanced chemical research will vanish. From a man of ability he has sunk into the hardly able class in the eyes of the chemical world.

Lest some one surmise that these statements arise from an overdose of committee work during my university service, let me set his conjectures at rest; during fourteen years' residence at one university I served on only one committee. I recall it well, it was a military committee of some sort. After a few meetings, at tea and crackers, I observed that one professor had a penchant for conversation and debate which eventuated in the elimination of all other views but his own. These same analytical results were obtained by a few of my friends on the committee, but out of respect for the president, board of regents, governor of the state, and others, they did not refrain as I did from attending subsequent meetings. Now, of course, I had just as much respect for all these dignitaries but I felt they had just as much for me and would not mind if I chose in preference the stinks and smells of my natural habitat. I did, though, sign the voluminous document—a report, I think, they called it—and actually did keep my promise to attend the otherwise soporific faculty meeting where it was read. I recall further that I was invited to serve on one other committee, but the only hour I could get free was 11 P. M., and that was too late for tea and crackers, which was over at nine.

No one can deny this frightful waste of valuable time among our professors at a university. There are exceptions, of course, but the general condition is exactly as I have portrayed it. I am forced to characterize this condition as a crime, but more often it is styled as the university evil. Many university men will tell you it is a part and function of university service. Those who really know will tell you it is a part and function of university non-productiveness. The condition naturally did have its inception in that period where a few men alone constituted the entire working mechanism of a university. But to-day when every university is organized more or less upon a rational basis, why are we cursed with this primeval practice? If we accept it as academic custom, then away henceforth with such obsolete custom. The cause of this evil is not far to seek, simply this: The non-recognition of ability as subservient to energy and enthusiasm.

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[1] *Collier's*, January 10 (1920), p. 36

THE TEACHER PAR EXCELLENCE

I must not, however, overlook the teacher par excellence. In the college and high school, his position is paramount and rightly so. Teaching for itself alone is his aim in life. Through close association with productive minds, he may reflect in classroom the best spirit of the day. His service in colleges and college departments of universities will ever command the greatest respect and appreciation, but in the graduate and technical schools of a university, as the seats of highest learning, he can play but minor part. The greatest inspiration to wide-awake students will ever come from the productive professor no matter whether he lectures or rambles in the classroom. In the ideal university, therefore, the non-productive professor, usually of the leisure class, will best devote himself to service in clerical and curule capacity outside of the four to eight actual hours per week required of him in university teaching. The ideal professor thus freed from detail and retarding influence of his non-productive colleague could then march steadily forward to the glory of himself and the university. Though these ideal conditions are far from realization, there are many professors who actually accomplish much of value in the realms of advanced thought. You will ever find them among those who shun this routine side of university life. Imagine, for example, the title of the clerical professor suddenly changed to read Chief Clerk of Committee on Attendance. How quickly he would resent this correct appellation, and yet this is his true category. He masquerades only under the title of professor and, due to his inactivity in what he professes, chemistry to-day at the university is no longer keeping pace with its advance in the industries.

IDEAL CONDITIONS FOR RESEARCH

If this deplorable condition is what we desire in our universities, then there is no point in my discussion. I am convinced, however, that the university is the proper place for research in pure chemistry. The conditions at the university which should make for quiet, undisturbed study, and rich and abundant association with minds alert in chemical and allied sciences, offer the very best opportunities for the development of the true chemist. The young man develops thus in the broadest manner and his outlook is characteristically broad. His subjects for investigation should be purely scientific and not necessarily commercial. The industrial chemical problems ought not to be overly emphasized in the earlier years. The closer the young man keeps to the pure science itself the better for him, the better for the universities, and the better for the industries. When, later, he may choose to enter industrial work he will find his training none amiss and his breadth of view most highly serviceable. It is here that I must firmly maintain that those young men who jump into industrial problems too soon after graduation have little or no chance of broadening their general knowledge of chemistry. The tendency to specialization is too well marked even in the industrial world. Everywhere you will meet with young men who realize this all-important fact. Their opportunity for broader development is past. It is not likely to return. Discouragement is easily discernible in their features. Had they but known of some plan upon graduation which would have offered a chance for pure research with a real live hope of remuneration, that chance would have been seized forthwith. Whatever the result, the better self of that future chemist never could deprecate his early ventures, and corresponding content would characterize now his daily endeavors.

Through the planning of researches and publication of results the science as a whole will advance. Chemical self-confidence is obtained no more readily and decisively than by publications, for these stand out as theses which the author is ready to sustain before a world of chemists. Indeed, this side of research may after all appeal so strongly to the young man that he will choose to continue it in the university setting. His gradual rise to a professorship with research ever his goal will inaugurate an era of greatest chemical activity in America. We have at present all too few of this type, so few that they are almost lost amid the multitude. I have never been able to see any other form of investigation in chemistry than that of pure unadulterated research, for itself alone, with no thought of service or utility, as anywhere near so broadening in its influence upon the student's development. The university is, of course, the proper place for such studies and I deduce from the considerations above my third premise: *There is the greatest possibility for advancement in pure chemistry in the investigations undertaken in a university or endowed laboratory.*

It should be clearly emphasized that I am not criticizing the research at special institutions and at industrial research laboratories. The young chemist graduate, however, when situated in these positions has not the freedom to browse about to his liking and strike out where his fancy leads. The atmosphere of the university almost overstimulates this freedom, but the results cannot be other than encouraging for the future of the science.

Upon the three premises already discussed my fourth premise finds support and may be stated as follows: *The industries will profit most in a general way from the published investigations in pure chemistry issued from the university and endowed laboratories.* Naturally, the industries will profit by their own advanced researches. The scientists though who conduct these researches must ever keep in touch with advanced thought. New ideas and new methods as elucidated from various investigators are seized with greatest zeal and thus almost a direct good results to the industrial organization through the advances made in the pure science. So firmly am I convinced of this that I feel it my duty to draw attention of chemists everywhere to the golden opportunities that manifest themselves for furthering this devotion to pure chemistry. They will not develop by themselves. The road is too difficult and encumbered with many hazards. My conclusion, therefore, to the four premises I have drawn is simply this: *The universities, the industries, and American chemists must encourage the further study of pure chemistry by the young graduates of our colleges.*

MONETARY REMUNERATION FOR SCIENTIFIC CONTRIBUTIONS

I have consumed so much time in the statement of basic troubles that I shall merely outline the plan which I believe is adequate in all respects. I would have the royalties paid to authors for books and magazine articles paralleled in some form for those who publish original chemical contributions in our representative chemical journals. These contributions need not be confined to any one branch of chemistry. They should be all-comprehensive. The only criterion for consideration is their mark of originality.

In detail I should suggest that the three most interested parties contribute in every way possible to encourage chemical research. Thus, a group of universities, a group of industries, and the AMERICAN CHEMICAL SOCIETY might share in this contribution. It cannot be assumed that these three interested groups will contribute equally, but each in itself may assist directly in the remuneration which I believe the contributors should receive. First and foremost, the several Boards of Editors of the AMERICAN CHEMICAL SOCIETY should be willing to serve as judges upon contributions received. When an article is accepted, the author or authors should receive at once an immediate award or honorarium. The amount possible must of course depend upon the resources at hand and, more directly, upon the size of the endowment which we hope can be established in the SOCIETY for this purpose. Naturally without such endowment, the SOCIETY could not encourage expenditures in this direction. From the university in whose honor the contribution was made, the author cannot expect to receive any monetary remuneration other than the continued supply of needed resources for actual work. Public recognition, however, of each contribution should freely be accorded but the university will best honor itself and the young authors by establishing a title of honor directly attainable upon publication of some ten to twelve researches; thus such title as "Assistant Director of Research" would amply gratify the young man who was working for the advancement of science. Their former title might still stand as a "Fellow," "Assistant," or "Instructor," but when it is actually possible to earn a title by real work, you can appreciate how much more valuable the entire framework of a university career would loom up in the eyes of thinking men. After another ten to twelve researches, the contributor may well be given the title of "Director of Research." The overabundance of non-productive chemists in our universities would, I assure you, most clearly be demonstrated by such a procedure. Naturally, our chemical drones will object to these suggestions, but I doubt if any university will weigh their objections seriously. They have so little influence in the chemical world that they must sooner or later lose all influence in the academic world.

INDUSTRIAL ORGANIZATIONS WILL FINANCE PROPOSITION

The real financial remuneration for the articles accepted must come, undoubtedly, from some industrial endowment. It would seem best to make only a portion of this subject to award on the part of the AMERICAN CHEMICAL SOCIETY. The larger portion should remain intact and should be subject to award by a committee properly elected by the industries concerned. Upon notification by the Boards of Editors of the AMERICAN CHEMICAL SOCIETY of the award of an honorarium to some author for a contribution of original research, this industrial endowment committee should award the author a proportionately larger sum and thus the findings of our editors may be made the criterion for the second allotment. For example, let us suppose the editors voted an honorarium of one hundred dollars from their share of the industrial endowment. The industrial endowment committee might then be able to quintuple the award and thus six hundred dollars could be sent to the author at once. This is, I assure you, none too small a recompense when we consider the annual royalties paid by publishers to authors o our second and third rate textbooks.

RESEARCH MEN DESERVE BEST REWARDS

The critics of my plan will naturally jump at the opening I leave; namely, monetary award for scientific endeavor. "The honor of contributing to our JOURNAL should suffice alone as recompense." To this I can answer now but briefly: You speak of by-gone days. Here and there a young man will turn his fancy into research with little thought of to-morrow; the best men, the live men, the men who have the mental grasp for bigger things, will not tarry too long where life is difficult and honor shallow. A world of endeavor surrounds us all and we must join in the quest or remain as useless adjuncts of a forgotten past. No matter how our philosophers may wail, they can no more change the trend of endeavor to-day than a firefly can change the temperature of a mighty iceberg.

Young chemists everywhere may here find a really practical way in which to devote themselves to research. They must have some incentive else only the weak will be left to carry on the university work. The strong may just as well develop in one direction as in another and the plan I offer is simply one to induce the best types of minds to try their fortune at pure investigation for itself alone. Our journals accordingly should overflow with good material. But I can well imagine the thunderous protests that will resound from pseudo-chemists who will fear gravely that a mass of worthless material may find its way to publication. Our editors, however, are chosen for their ability and are representative of the best American chemists. I should not lose confidence in them. Just let the pseudo-chemist contribute a trifle now and then himself. It is usually his type who will find the most worthless data. What we wish is everything that savors of originality and I assure you the mass cannot be too voluminous to bother for a moment our industrial specialists. If we must wade through oceans of data, the mere chance of finding an isolated and much-valued pebble on some far-off beach will well repay us. According to this plan, you will note how both instructor and professor, how both college graduate and assistant come into the same consideration. The title of the chemist is supernumerary, the results only will count. Possibly the older professor may be awakened to the opportunities that confront him and ideas almost dormant may be brought into the light of day. Certainly the young graduates will find herein an excellent means for further development. The assistantships at a university will suddenly be enhanced in value, for these positions can well be held by men intent upon research. The small livelihood which an assistantship affords will be amply sufficient to start the young men on their course. In fact, it is to be hoped that a greater number of assistants in our laboratories can be honored by an opportunity to work under the direction of productive men. There is nothing so demoralizing about a chemical laboratory and nothing so detrimental to the spirit of research therein as the presence of an aimlessly drifting assistant. If all assistantships could be offered primarily to young investigators, I feel confident there soon would be need of devising some scheme for receiving and weighing applications from young men intent upon pursuing advanced work at the various universities. With increased competition in selection of graduate assistants who actually are more effective than most professors in laboratory teaching, the overabundance of dead professorial timber may finally be eliminated, to the good of the university and of the science.

Just how far this plan ought to be extended, if ever put in practice, would be a matter left to the endowment committee. Though I have had only the young assistants and instructors in mind, I see no reason why it could not be equally applicable to the full professors. Certainly they should receive a monetary recompense for their services—no matter whether or not the old, moss-grown ideas of honour alone as recompense still obtain in their circles. The entire plan appears, upon closer analysis, to be the counterpart of that ideal industrial fellowship heretofore described as a fellowship nowhere existent but one that might be granted to young chemists through competitive examinations and then placed in operation at whatsoever university the fellowship holder selects. Such ideal industrial fellowships naturally entail the services of an examining board for the applicants and this board indeed might serve for many industries. My plan simply eliminates all examinations and accepts the findings of the several Boards of Editors as a final criterion of merit. The recompense may thus be construed in the same sense as that for an ideal industrial fellowship—but with a distinction that is distinct; namely, the money is paid only upon the accomplishment of something worth while and not thrown around helter-skelter among doubtful candidates in pleasantly located laboratories, hoping for something to happen.

This plan of reward for meritorious research comes now as a further bestowal of honor upon those fellowship holders who would offer original contributions to science. Throughout my discussion you will find this plan—the plan of incentive—ever adds to the good things that are and detracts from the bad that persist. The system certainly offers possibilities far beyond what I have pictured.

I see in this plan no adverse turn. It should accomplish what universities have long desired. It should instill in the young men that desire for research which teaching alone is slow to impart. It should open to industrial scientists the possibility of further study in special fields under the direction of some prominent university man. Through this advance in the study of pure and applied chemistry, the entire chemical activities of America will march forward in steady progress.

In substantiation of my selection of the three most interested parties, I scarcely need explain the interests which representative universities will ever take in problems of research; technical schools and institutes of research naturally fall into the same group. Industrial organizations already realize the importance of scientific advance as directly stimulating their activities and instilling new spirit into their investigations. In a far broader sense and with correspondingly greater responsibility do I view the interests of the AMERICAN CHEMICAL SOCIETY in the advancement of research in America. Having grown with prodigious strides into the greatest society of its kind in the world, is it not fitting that we launch some project that will return to port laden with scientific production—the most valued treasures in this world of progress? To this end, I earnestly hope our several Boards of Editors will consider my proposal in its several aspects—more poignantly from the standpoint of increased duty in judicial capacity. If our Directors and members of the Council will then approve the expenditures of money to this purpose, I assure you the industries will gladly espouse a cause so heartily endorsed by these several groups of scientific men. Many universities, I believe, will aid in every way possible a step that will make for the enhancement of all those lesser positions now so poorly filled. Any reward of honor naturally will come slowly, but I believe it will come surely.

The universities should lead in scientific thought and endeavor. The difficulties in chemical art should best find their solution in university circles. Thus the universities may be dependent upon the industries for the revelation of reactions so little understood, and again the industries should ever be dependent upon universities for leadership both in scientific development and in the broadest intellectual development of the young college graduates. Both university and industry must benefit through mutual progress, and as thus interdependent may they ever be of greatest assistance the one to the other.

THE RELATION OF THE CHEMIST TO THE UNITED STATES PHARMACOPOEIA[1]

By Charles H. LaWall

CHAIRMAN, REVISION COMMITTEE, U. S. PHARMACOPOEIA

The United States Pharmacopoeia this year celebrated its centenary, the first issue of the work having been published in 1820. It is the second oldest national Pharmacopoeia in the world, the only older one being the French Codex, as the corresponding work is called in France. It was originated by physicians, and the statement of the reasons for its beginning made in the preface of the original 1820 edition is essentially true to-day, as will be seen by the following quotation:

> It is the object of a Pharmacopoeia to select from among substances which possess medicinal power, the utility of which is most fully established and best understood, and to form from them preparations and compositions in which their powers may be exerted to the greatest advantage. It should likewise distinguish those articles by convenient and definite names, such as may prevent trouble or uncertainty in the intercourse of physicians and apothecaries.

It was planned at the beginning to revise it every ten years, and this has continued up to the present time.

In the 1830 edition the help of apothecaries was acknowledged, and in 1840 the pharmacists were requested officially to aid in the revision of the work. When the first Pharmacopoeia was issued in 1820, there were no separate schools of chemistry or pharmacy and few chemical manufacturers. Most pharmacists were chemists and some of them like Scheele, Vauquelin, Pelletier, Caventou, Serturner, Derosne, and others, had made discoveries of moment.

The earlier editions of the Pharmacopoeia, therefore, contained a large number of methods for preparing chemical substances now manufactured only on a large scale and never at present prepared in the small way for commercial purposes. Among these may be mentioned:

Citric acid—from lemon juice.
Ether (then called sulfuric ether)—from alcohol and sulfuric acid.
Water of ammonia—from ammonium chloride, lime, and water.
Ammonium carbonate—from ammonium chloride and calcium carbonate.
Silver nitrate—from silver, nitric acid, and water.
Bismuth subnitrate—from bismuth, nitric acid, and water.
Mercuric chloride (called oxymuriate)—from mercury, sulfuric acid, and sodium chloride.
Mercurous chloride—from mercuric chloride and mercury.
Sodium bicarbonate—from sodium carbonate and carbon dioxide.
Zinc oxide—from metallic zinc by oxidation in a red-hot crucible.
Processes for manufacturing morphine and quinine were also included in some of the early editions.

These will indicate that the pharmacist of those early days had to possess chemical knowledge and manipulative technique of no mean order. There was little or no attempt to standardize substances except in such a crude way as is shown under hydrochloric acid, then called *muriatic acid*, in which it is stated that "a fluid ounce should dissolve 220 grains of carbonate of lime."

The usefulness of pharmacists upon the Revision Committee of the Pharmacopoeia was so apparent that by 1880 they had begun to predominate, a condition which has continued down to the present time.

The United States Pharmacopoeia of 1880 may be said to be a turning point in its history, for by this time manufacturers supplying chemicals of all kinds were common enough to enable some of the processes for manufacturing chemicals to be dropped and to require more thorough consideration of scientific standardization. The change then begun has developed until at the present time the Pharmacopoeia is largely a book containing the approved nomenclature, descriptions, and standards of substances which are used in medicine and the processes are limited to those mainly for galenical preparations, *i. e.*, the liquid preparations of vegetable drugs, such as fluidextracts, tinctures, etc., and also for the simpler chemical solutions.

The personnel of the Committee of Revision has likewise changed—originally composed of physicians only, later of pharmacists and physicians, the committee of fifty who revised the tenth edition (ninth revision) in 1910, which is official until the work of the convention meeting in May 1920 is completed, included physicians, pharmacists, chemists, biologists, pharmacognocists, and other workers in specialized lines. Inasmuch as nearly one-half of the 782 official substances may be classified as chemical substances, there is a comparatively large group of chemists on the present Committee of Revision. I believe that over 20 per cent of the fifty members are members of the AMERICAN CHEMICAL SOCIETY and several of these have been prominently identified with that organization for years. The United States Pharmacopoeia is not a work of interest solely to physicians and pharmacists. In the Federal Food and Drugs Act and in the corresponding laws of many states, its standards are recognized as having legal authority.

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[1] Presented at the April Meeting of the Philadelphia Section of the American Chemical Society.

The business management of the Pharmacopoeia is vested in a Board of Trustees of seven members who, with the Committee of Revision of fifty members, are elected decennially from the delegates who assemble in Washington on the second Tuesday of May in the years whose figure ends in a cipher. These delegates constitute a convention in whom the ownership of the Pharmacopoeia is vested and which is now a chartered body. The delegates mainly come from medical and pharmaceutical colleges and societies, but the American Chemical Society is one of the organizations regularly authorized to participate, as are also the various departments of the United States Government whose work bears any relevancy to medicine or pharmacy.

WILLARD GIBBS MEDAL AWARD

Brief mention was made in the June issue of This Journal of the presentation of the Willard Gibbs Medal to Dr. Frederick G. Cottrell, recently appointed Director of the U. S. Bureau of Mines. It gives us pleasure to reproduce below the admirable address of the recipient of the medal, and Dr. Whitney's remarks in presentation.—[Editor.]

PRESENTATION ADDRESS

By W. R. Whitney

Dr. Cottrell, in presenting to you this medal on behalf of the Chicago Section of the American Chemical Society, in memory of the great Gibbs, I am not going to recite a list of your well-known achievements. This is not merely because these achievements are so well known, but because I prefer to preach a brief sermon.

I choose to call attention to your *process* rather than your product. I believe that the *way* you have done things is even more important than the actual things themselves. Our country might get along without the particular products of your effort, but it could not get along without men personifying your procedure. We are not so much interested in recovery of fumes, the abatement of the smoke nuisance, in the saving of silver, zinc, or sulfuric acid, in the production of helium, or any other of the definite undertakings which are attributed to you, though these are in themselves very valuable, but rather we exalt that human *quality* which insures advanced undertakings of public welfare and interest. You are one of those who intelligently decline to proceed along entirely old paths but map out and push along new ones. You are one who, no matter how wisely you may act, must withstand many rebuffs and disappointments, because, in blazing new trails, countless obstructions must be encountered and surmounted. Herein you have always retained your momentum and your good nature. All our improved ways of living, our broadened views, our greater activities, and our increased pleasures are due to new and difficult steps, often seemingly absurd when judged by us who are impelled by habit only. In tilling new ground and in opening unbeaten paths you have needed your well-advanced scientific education for keeping high your coefficient of success; a splendid personal quality of open-heartedness and a carefully controlled physical constitution. All of these you have clearly and unselfishly devoted to the public good. You have not been satisfied to accept things as they were, and we chemists highly appreciate ideals and those new ideas which, while not at first acceptable to the average man, can be made so by human effort. Your support of one universal language may be looked at as only a few years too early, but it is a type of the thing for the realization of which people will have to depend on someone like yourself, if it is ever to be realized. Your work in the West and your radical undertaking in the East, in establishing the Research Corporation, together constitute a trail blazer which calls attention to the possibilities of coöperative research and to the position of our Government in relation to ideas and inventions of its employees. You have started something which may well grow far beyond your anticipation. You have set an example not only in accepting the responsibility of such public work, but your patient persistence in carrying out your own plans with support which only your well-known integrity, industry, and enthusiasm could insure, forms a new high plane of activity for the emulation of the American chemist.

We are glad that you have been added to that group of chiefs of the Bureau of Mines, Holmes and Manning, which our Government has so fortunately possessed. We will be willing to forgive in you many possible errors or mistaken undertakings in the future, if your ideals and your will to be right and the intuition to be constructively dissatisfied with imperfect existing conditions, persist as they have hitherto existed.

MEDAL ADDRESS
INTERNATIONAL SCIENTIFIC RELATIONS

By F. G. Cottrell

The experiences of the war have served to illustrate as never before the importance of the position held by the scientist both pure and applied, not only to our daily life at home, but also in international affairs, and during the war perhaps no branch of science carried a more important load or gave a better general account of itself than did chemistry in all its various branches. The details of chemical war work have filled a good part of our journals for so long that to dwell on them here would be bringing coals to Newcastle; but what the chemist's part is to be in the reconstruction period upon which the world is entering still lies before us and has a most legitimate and insistent call on our serious attention.

The war certainly furnished a great stimulus to discovery and invention, but from the standpoint of technical achievement it bids fair to have served only as the prelude to a vaster industrial development of truly international character which may reasonably be expected to follow in its wake. The stress and strain of the period we have passed through has awakened the imagination of the rising generation to a world consciousness as nothing less far-reaching could possibly have done, and we in this country are destined perhaps even more than those in Europe itself to feel the full effect of this swelling pulse, because to the European nations international contacts have long been matters of course and from a physical aspect almost as natural as intercourse among the states of our own Union. But this was a new experience to the majority of the 4,000,000 young Americans who just at this most impressionable age have been thrown into daily physical and mental contact with their fellows of foreign countries, as also the conditions and traditions of home and economic life in these countries. They have brought back with them a mental leaven which, though it may take some time to fully develop, and will undoubtedly require careful guarding against the wild yeasts of Bolshevism and other extraneous growths, should eventually make itself clearly felt as a tremendous power for good and for the broadening of the concepts of our national life both human and economic.

INTERNATIONAL RELATIONS FOSTERED

Chemists in this country, as a class, have recognized and fostered international relations probably as much, if not more, than have most of the technical and engineering professions. This is perhaps due in no small part to the very close and cordial coöperation which has existed from the first between pure and applied chemistry in this country, for it is usually easier to get perfectly free international coöperation in the pure sciences than in applied branches where questions of business expediency at once intrude themselves. But the chemists in the past have been remarkably successful with their undertakings in both fields; as, for instance, the International Committee on Atomic Weights on the one hand and the International Congresses of Applied Chemistry on the other. Even the primarily social side has found its expression in the systematic exchange of courtesies between such organizations as the Chemists' Club in New York, which has come to be really a national rather than local institution, and the more recently established Chemical Industry Club in London, while beyond there is already the foreshadowing of a similar club among the French chemists.

The fact that the Chemists' Club in New York avowedly embraces in its membership all fields of chemistry, both pure and applied, while even in its name the London club emphasized the distinction between the academic and the industrial phases, emphasizes a rather clearly marked difference in point of view between chemists in this country and abroad.

In this country we have come to accept so tacitly as almost axiomatic, the close coöperation of these two divisions of the profession, that we may easily fail to appreciate how questions of this kind appear to our friends across the water, and the difference in historical background underlying this. Yet if we are to work most effectively with our foreign colleagues we must acquire a sympathetic understanding of their points of view, whether we entirely agree with them or not, and where we do not agree let us hope we will restrain ourselves sufficiently to avoid unduly adding to the partly justifiable and now rather widespread impression among Europeans that so many Americans feel themselves thoroughly competent both from experience and native ability to come over and quite *de novo* reorganize European civilization on a (to them) thoroughly satisfactory basis.

Frederick G. Cottrell, Willard Gibbs Medalist

Lest I leave an unfair and misleading impression with you, I should perhaps add that this aloofness between the pure and applied sides of chemistry abroad shows some signs of gradually abating, as was clearly evident to those of us who participated in the organization of the International Chemical Council at the meetings in Paris, London and Brussels last year.

A significant illustration of this is also to be found in the history of the Société de Chimie Industrielle de France organized during the war. At the outset the newcomer was looked upon with a good deal of anxiety by the old established Chemical Society of France, which naturally and historically represented primarily the academic side of the subject and was controlled largely by chemists in academic positions. Their chief fear was apparently that the creation of the new society and journal would only serve to scatter and dilute over too wide a field the meager funds available to the chemists as a whole for organization and publication purposes, and thus weaken the entire structure. As a matter of fact, however, the new society and its journal "*Chimie & Industrie*" have, under the able and broad-minded leadership of Paul Kestner, the society's first president, prospered from the very start, and, instead of dividing and weakening the support of the older society, have brought in such a wide range of new interests and given such stimulus to French chemical industry in general that both societies are profiting by it.

Those responsible for the guidance of the new society have definitely and officially taken the constructive and liberal stand that since pure science is fundamental to industrial science, but the latter is naturally more closely associated with the material returns and with the interest of the public generally, it has a moral responsibility to help the academic organizations to maintain their high standards of scientific work and independence of industrial considerations.

Due to entirely different traditions and circumstances existing in France, it would not be easy or probably desirable, at any rate for the present, to merge the two branches in one large society and single group of journals as we have them in this country, but the French are rapidly working out their own methods of close and cordial coöperation which will undoubtedly fit their needs as well as our form of organization meets our own.

Great Britain, as you well know, has had her strong Society of Chemical Industry for many years and there has long been a fair degree of coöperation between this and the Chemical Society of London as well as other academic groups, but as a result of war emergencies these, as well as other bonds between various special groups both on the pure and applied side of chemistry, were strengthened and to a large extent centralized through the creation of the British Federal Council for Pure and Applied Chemistry. Much the same processes have also been working in other countries, but the above serve sufficiently to show the general tendency of the day, the great importance of which, for the subject in hand, lies in the greater facility which these broadly comprehensive national organizations furnish for effective international coöperation.

PROTECTION AGAINST MISUNDERSTANDINGS

If international coöperation in science can be made effective in both the pure and applied branches it will unquestionably furnish one of the most powerful forces possible against the growth of national misunderstandings. It is, of course, easier for the devotees of pure science to work freely together than for those more closely associated with the business relations of their subjects.

Secrecy, however, even in business relations, if not disappearing, is at least rapidly coming to be viewed generally from a very different standpoint than heretofore, and it is interesting to note how this change began and first received official recognition on the distinctively scientific and technical side of business, *viz.*, in the matter of patents of invention, the government offering the inventor certain definite legal regulation and protection in lieu of his secrets if he would make these latter frankly and fully known to the public. At the time our patent system was created, few, if any, would probably have been found who could have clearly seen foreshadowed in this even as a distant possibility, the necessity or the justification for the publicity of purely business details of railroad operation, with which the Interstate Commerce Commission has since been charged. This step, again, was recognized in the special case of the transportation companies and other public utilities corporations long before people were ready to consider the extension of similar ideas to other lines of business. Thus the creation of the Federal Trade Commission came many years after that of the Interstate Commerce Commission, though in the broad economic sense the greater part of the work of the Interstate Commerce Commission, as well as many questions of patent administration now left chiefly to the courts, logically constitute only special branches of the general subject for whose study and guidance the Federal Trade Commission was established, *viz.*, the maintenance and safeguarding of fair trade practices, including the regulation of monopolies in the public's interest.

The fact is that as the civilized world progresses and we accept the benefits of that developing civilization, we are less and less able to live to ourselves alone. What was so nearly a man's purely private affair when his business was small, becomes with the growth of that business itself so much more largely a public concern that we may very properly recognize the need eventually for a certain readjustment in the distribution between the individual and the public both of interest in, and responsibility for, the conduct of that business.

These same problems must eventually enter in principle at least into the consideration of the international questions which are rapidly being forced upon our attention. Fortunately, however, very few of these latter are apt soon to reach a stage where detailed legislation must be undertaken, but in working out the corresponding national phases of the same problems we should at least have in mind the desirability of building up an intelligent public interest in the international aspects of the subject.

RESPONSIBILITIES OF THE SCIENTIST

The order of approach in the international phase is apt to be much the same as in the national, which again inevitably places special responsibilities upon scientific and technical men. Thus, at the meeting of the Engineering Section of the International Research Council in Brussels last July, the chief subject of discussion was the possibility of working out some form of international patent which would gradually tend to unify the present wide divergence in patent procedure among the different countries and also to lighten the burden both of detail and expense upon the patentee. The opinion was pretty clearly brought out at the meeting that it would probably not be practicable even if desirable to secure any essential changes in the patent laws of the individual countries as an immediate result of such a program, but that the effort should be made rather to secure a central international office where the specifications and claims might be gotten into a standard form acceptable to all of the countries and the novelty and patentability of the invention or discovery determined as far as possible by an examination somewhat similar to that made in our own patent office, but of wider scope with reference to foreign laws, publication, and practice. This would then be filed in the countries selected and would be subject in each to the laws governing patents therein. It was hoped, however, that all the countries would coöperate in working out the procedure of the central office and that this in turn would have a tendency to react upon the development of their own patent system, at least in so far as gradually adopting reciprocal relations in regard to the treatment of these international patents.

It was generally felt that coöperative international effort of this kind would have a very stimulating and salutory effect on the patent system of the individual countries involved. Here again, this should be looked upon as a matter of interest, not merely to the technical man and the inventor, but one in which the academic scientist should also take a part. The spirit of our patent laws clearly holds that a patent to be valid must be a true and full disclosure of the novel discovery or invention claimed, but it is too often the evident intent of the patentee or his attorney to give only as little real information as he feels is absolutely necessary to fulfill the letter of the law. If more genuinely scientific work were published by scientists of standing and ability in the form of patents, even if also published elsewhere, it would have a very much to be desired effect in raising the general tone and standard required in this respect in patent specifications; for patent examiners and courts are after all human, like the rest of us, and we are all influenced, if not even compelled, when placed in a judicial position, to set our standards with some reference to the average of the material available.

SPREAD OF THE METRIC SYSTEM

Turning for a moment to the matter of standardization of weights and measures: This is, of course, one of the oldest and best recognized fields for international coöperation, and here again the scientists have led the way. The use of the metric system is now essentially universal in pure science, and is making good headway in the newer branches of technology; such as chemical and electrical engineering, and to a considerable extent in mining and metallurgy, but in mechanical and civil engineering, especially where these touch, respectively, land surveys and diversified manufacturing, the greatest opposition to change is naturally to be found. While my whole training as a chemist naturally gives me the strongest possible prejudice in favor of the metric system, and, viewed from the international side, I see nothing else in the field having any chance of final worldwide adoption, it yet seems to me that in this country at least for the present, reform should still be sought more through education and example than by resort to mandatory legislation. We already have legislation permitting and encouraging the widest possible use of the metric system in all its details throughout the whole country. It must be remembered that mandatory legislation touching as broad a field as this, and so ramifying into every detail of the daily life of every individual, can only be really successful in attaining its object if its enactment is preceded by a thorough awakening of interest in the public mind and a real appreciation of the question at issue. This statement should not be construed to mean that the present rather widespread agitation for mandatory legislation in Congress on the use of the metric system is producing no useful result. On the contrary, I am inclined to think that entirely aside from whether any of the legislation sought is eventually secured, the effort expended will be beneficial by maintaining a focus of public interest and discussion upon the whole problem of international units and standardization of technical equipment generally.

The metric system goes a long ways toward international standardization, so far in fact for the purposes of the chemist that he is apt to overestimate its relative significance in, say, the field of mechanical engineering, where to-day probably the greatest inertia, not to say, opposition, exists with respect to its general adoption. The chemist is dealing for the most part merely with quantities of matter in bulk. He could change his weights and measures and go over in almost any chemical factory from any other system to the metric, and *vice versa*, almost overnight, without a single change in his machinery except for the scales and measuring appliances themselves. Whereas, if his master mechanic were forced to do the same thing with regard to all his tools and repair parts, it would mean practically a complete rebuilding of the factory. Nor would the mere general adoption of the metric system completely solve the mechanical engineer's problem of international standardization. Take as fundamental a matter as screw threads. Each country, and one might almost say, each industry, has adopted its own shape and standard pitch. With this, and many other similar discrepancies staring him in the face, is it any wonder that the manufacturer of mechanical equipment has a tendency to view the metric system in its present stage of development as only one bite at the cherry, and to ask himself whether, in view of the changing of all his patterns, and jigs, and machine equipment in this one respect, when there are others just as important awaiting later consideration, it is not like cutting off the dog's tail by degrees?

GENERAL INTERNATIONAL STANDARDIZATION

Do not misunderstand me as arguing against the adoption of the metric system, but rather for a wider and more comprehensive application of its fundamental conception of general international standardization, even if in so doing, our progress for the moment may seem to slacken somewhat.

What is needed most is a wider, stronger, and more closely interwoven network of international, scientific, and technical organizations, working earnestly for better understanding and coöperation between all concerned for the purposes of the common needs and common good of humanity as a whole, and fortunately, the spirit of the times gives good promise of real and rapid progress in this direction.

DEVELOPMENT OF AN AUXILIARY LANGUAGE

In his introductory remarks Dr. Whitney made reference to my interest in the problem of an international auxiliary language. Even here we have an interesting illustration of how prominent a part the physical scientist has played in international projects even so far removed from his own direct field as the problem of language would seem to be; for closely linked with the history of the Esperanto and Ido movements we find such well-known names as Lorenz, Bourlet, Ostwald, Ramsey, Donnan and Morse, while last year in London and Brussels it was among the members of the chemical group that the project first took shape to secure the appointment by the International Research Council of a committee "to investigate and report to it the present status and possible outlook of the general problem of an international auxiliary language" and "to coöperate in its studies with other organizations engaged in the same work."

This has already led to the authorization of similar committees by the British and the American Associations for the Advancement of Science, as well as a definite movement in a number of our leading universities to take up the problem not only from the purely linguistic aspect but even more particularly from the side of sociology, psychology, and pedagogy, since as a matter of research these latter departments find a more fertile and interesting field for study than do even the linguists. In fact, if we are to have synthetic linguistics as a seriously recognized subject we must probably develop a new type of linguist for it, just as the coming of physical chemistry necessitated the development of a new kind of chemist. Why, it may be asked, should the scientist take more interest in this problem than the linguist? For answer, one may point to the development of stenography and ask where it would be to-day if it had been left to the linguist, for the fact is that the present type of professional linguist is interested almost exclusively in either the philological or the literary aspect of his subject and looks upon its purely utilitarian developments from much the same point of view as the extreme type of academic research scientist does upon the routine of applied technology.

What the scientist, and for that matter the business man and the man in the street, wants for international purposes is primarily not a literary language but a simple and serviceable code, bearing somewhat the same relation to the ordinary ideas of every-day life that the formulas of the chemist or the equations of the mathematician do to these specialists' own domains of thought. As a matter of fact, scientific terms are already practically international and so all that remains to be done is to bring the simpler and non-technical half of our concepts up to the same international standard of expression.

Here, too, we must again emphasize the auxiliary character of such a proposed international code language, since it is in no wise intended to compete with any national language except for purely international purposes, where the only desiderata are simplicity, clearness, and entire neutrality. Herein as a purely auxiliary tool it escapes completely from the type of opposition already discussed in connection with the compulsory adoption of the metric system.

Few realize how much real progress has been made and how much tangible material as the basis for a critical study of the general problem has already been accumulated in this field. Thus at the outbreak of the war there were, for example, about a hundred journals being published in Esperanto alone and over half this number survived the cataclysm and are still appearing, with new ones being constantly added, especially from the newly created states, and suspended journals gradually resuming publication.

However it is not my purpose to go into details here, but merely to use this subject as a suggestive illustration of how wide and fundamental are even the apparently incidental contacts of the scientist with these larger world problems.

SOUND INTERNATIONAL POLICY

In the above I have confined myself chiefly to what might be termed the intangibles, because in casually thinking of the subject we are perhaps more apt to overlook these. However, from the material side the chemist's responsibilities are, if anything, even greater and more specific. Whatever the political excuses given, in reality more wars have probably centered about the control of raw materials than any other question; and who is there better equipped than the chemist to look into the future with regard to the world's needs for raw materials? He it must be who will ultimately advise our statesmen as to these basic facts upon which alone a sound and just national as well as international policy can be built. In this regard we are certainly at the parting of the ways, as discussions and negotiations all over the world clearly indicate. The petroleum situation perhaps occupies for the moment the center of the stage and well illustrates how a single raw material may become the pivot on which the whole international situation turns.

Petroleum and natural gas in this connection immediately suggest helium, which, though almost the antithesis of petroleum as regards its scarcity, is commanding nearly equal international interest on this very account, coupled with its unique military importance. Thus far we have in this country the only developed large natural supplies and the only other known source which as yet promises to be significant lies to the north of us in the hands of our friends, the Canadians. The newness of this whole subject and the intricacy of its relations to both war- and peace-time aviation present problems of national and international policy in whose decision the advice of the chemist and engineer must necessarily enter with great weight.

Petroleum and helium are only two examples picked almost at random from the multitude of available material already familiar to you, but they serve well to illustrate the point I set out to emphasize; namely, how responsible and important a part the chemist must take in the guidance of new international relationships now rapidly pressing upon us.

CHEMICAL READING COURSES[1]

Prepared by the Committee on the Preparation of a Recommended List of Chemical Texts for Libraries
W. A. Hamor, *Chairman*, L. C. Newell, A. M. Patterson, W. Segerblom

ELEMENTARY OR INTRODUCTORY CHEMISTRY[2]

The facts and principles of chemistry are available for all who will take time to read. But do not conclude that the essential facts and leading principles of chemistry are buried deep in technical journals and heavy textbooks. There are many interesting and reliable books on chemistry written solely for those who have not made a special study of this science. Hendrick's "Everyman's Chemistry" (Harper, 1917; 374 pp.) is a lively account of modern chemistry. This book is "designed chiefly for those who declare that they do not understand anything about the subject." Another book written for the general reader is Philip's "Romance of Modern Chemistry" (Lippincott, 1910; 348 pp.). It contains an absorbing discussion of flame, fuels, explosives, extremes of temperature, crystals, and the by-products of chemical processes. Still another is Slosson's "Creative Chemistry" (Century Co., 1920; 311 pp.), which describes in plain language such timely topics as cellulose, rubber, plastics, sugars, fats, and electric furnace products. Chemistry is so vast that you can read several similar books without duplicating topics. Hence you will enjoy two books by Martin: "Modern Chemistry and Its Wonders" (Van Nostrand, 1915; 358 pp.), and "Triumphs and Wonders of Modern Chemistry" (Van Nostrand, 1911; 358 pp.). Both books describe in non-technical language some of the recent striking advances in chemistry. Special topics are treated in Bird's "Modern Science Reader" (Macmillan, 1911; 217 pp.). This book consists of reprints of original articles by experts on such topics as the oxy-hydrogen process of cutting metals, combustion of coal, coal-tar dye industry, electrochemistry, and artificial silk.

CHEMISTRY HAS ITS HUMAN INTERESTS

Three books by Duncan should be read by everyone who wishes to know something about modern chemistry and its relation to human interests. "The New Knowledge" (A. S. Barnes and Co., 1905; 263 pp.) is a lucid account of the new physics and new chemistry in their varied applications. "The Chemistry of Commerce" (Harper, 1907; 263 pp.) is a fascinating interpretation of various phases of modern industrial chemistry. "Some Chemical Problems of To-day" (Harper, 1911; 254 pp.) recites recent contributions to theoretical and industrial chemistry. These books are written in beautiful language, which can be understood by the general reader.

Chemistry is a progressive science. Many commonplace facts are deeply rooted in chemistry. Going back many years we can find their origin and trace their growth. Tilden's "Chemical Discovery and Invention in the Twentieth Century" (Dutton, 1917; 487 pp.) is a vivid narration of the growth and progress of chemistry from 1800 to the present time. Sometimes its development is so rapid we can hardly keep pace with the movement. We need a survey of the field, especially in the application of what is sometimes called "pure chemistry." Findlay's "Chemistry in the Service of Man" (Longmans, 1916; 280 pp.) is a review of the world's indebtedness to the chemist, including applications of modern principles to chemical industries. Alexander's "Colloid Chemistry" (Van Nostrand, 1919; 90 pp.) is a summary of this interesting field of chemistry.

HEALTH AND SANITATION

The relation of chemistry to personal and public health is a vital topic. Bailey's "Sanitary and Applied Chemistry" (Macmillan, 1917; 394 pp.) treats of the atmosphere, fuels, heating, ventilation, lighting, purification of water supplies, disposal of sewage and household wastes, cleaning, and disinfectants. The book also contains many experiments. A more elaborate book is Baskerville's "Municipal Chemistry" (McGraw-Hill Co., 1910; 526 pp.). This is a compilation of a series of lectures by experts treating of such important topics as city sanitation, drinking water and disease, purification of water, milk, food adulteration, food inspection, street cleaning, smoke, textiles, paints, corrosion of iron, and cement.

Everyone has heard of radium, but not all realize the comprehensive inquiries conducted by chemists to find out the many secrets of this marvelous substance. A brief, accurate, and entertaining book on radium is Venable's "Radio-Activity" (Heath, 1917; 54 pp.). A larger work is Soddy's "The Interpretation of Radium" (Putnam, 1912; 284 pp.). This book is the substance of several popular lectures and is written in non-technical language.

Chemistry does not stand alone. It overlaps other sciences, especially physics. To understand part of the language of chemistry we need to read border-line topics. In Stewart's "Chemistry and Its Borderland" (Longmans, 1914; 327 pp.) physico-chemical topics are discussed. Talbot and Blanchard's "Electrolytic Dissociation Theory" (Macmillan, 1907; 85 pp.) treats of the theory of electrolytic dissociation, ions, and ionization in a compact, informative way. A summary of the work of the leaders in chemistry and physics during the last quarter of a century may be found in Jones's "New Era in Chemistry" (Van Nostrand, 1913; 328 pp.).

Chemistry grows so fast it is hard to keep up with it; hence sometimes we must resort to periodic reports. One of the best of these is "Annual Reports on the Progress of Chemistry" (Van Nostrand). These are epitomes of the progress of pure chemistry compiled by specialists selected by the Chemical Society of London and are indispensable for those who wish the latest data.

HISTORY AND BIOGRAPHY

Chemistry is essentially a human science. Its important discoveries are linked with the names of men whose lives are often like a romance. Some knowledge of the history of chemistry, especially of the great discoveries, is needed for an intelligent interpretation of the chemistry of to-day. There are scores of books telling about famous chemists and their work. One of the best of the shorter books is Thorpe's "History of Chemistry" (Putnam, 1910; Vol. I, 195 pp.; Vol. II, 202 pp.). It begins with the chemistry of the ancients and ends with contemporary chemistry. Many portraits add to its interest. Venable's "Short History of Chemistry" (Heath, 1894; 163 pp.) is a compact, brief book. Two other books covering the same ground, though in a different way, are Hilditch's "History of Modern Chemistry" (Van Nostrand, 1911; 273 pp.) and Armitage's "History of Chemistry" (Longmans, 1907; 286 pp.). The former contains a biographical index of chemistry and a chronology of chemical events since the time of Boyle.

We must not forget that chemistry is largely the product of experiments and that these experiments were performed by diligent men who worked much as chemists work to-day. Hence, there are many books devoted to the biographical side of chemistry. Roberts' "Famous Chemists" (Macmillan, 1911; 247 pp.) describes briefly the chief work of famous chemists and the part played by each in the development of chemistry. Muir's "Heroes of Science—Chemists" (Young, 1883; 338 pp.) recounts the progress of chemistry by incorporating selected biographies into a popular history of chemistry, while Smith's "Chemistry in America" (Appleton, 1915; 356 pp.) is a vivid story of the chemical pioneers in our own country; this book contains valuable and interesting information not readily found elsewhere. Thorpe's "Essays in Historical Chemistry" (Macmillan, 1902; 582 pp.) is a collection of biographies of about a dozen famous chemists from Boyle to Mendeléeff; considerable space is given to the French chemist Lavoisier, who laid the broader foundations of the science of chemistry. Ramsay's "Gases of the Atmosphere" (Macmillan, 1916; 314 pp.) is a narrative of early experiments and speculations on gases and of the author's discovery of argon, helium, and other rare gases in the atmosphere. Portraits enhance the value of the book.

Among the larger books devoted to the history of chemistry, which may be consulted or read in part, are "Chemical Society Memorial Lectures, 1893–1900" (Gurney and Jackson, London, 1901), Von Meyer's "History of Chemistry" (Macmillan), Muir's "History of Chemical Theories and Laws" (Wiley, 1907; 555 pp.), and Freund's "Study of Chemical Composition" (Macmillan, 1904; 650 pp.).

PERSONALITIES

There are many books about the life or the special work of a single chemist. The "Century Science Series" (Macmillan) includes in separate volumes biographies of Dalton, Davy, Faraday, and Liebig. No one should fail to read Tyndall's "Faraday as a Discoverer" (Appleton, 1894; 171 pp.)—a charming biography of a famous chemist written by a noted scientist. A discoverer's own account of his work brings us close to the man. Fortunately there are reprints in English of many original papers. Several are included in the "Alembic Club Reprints" (University of Chicago Press, Chicago, Ill.). In these little books Priestley tells how he discovered oxygen, Cavendish recounts his work on air, etc. Nos. 1, 2, 3, 4, 6, 7, 8, 9, 12, 13, 18 are the best.

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[1] Presented to the Council at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 2, 1919.

[2] By Dr. Lyman C. Newell.

OTHER BOOKS

This reading list is short. There are many other interesting books on chemistry, especially on single topics. Here is a supplementary list of a few more books you may wish to read:

Benson, "Industrial Chemistry." A condensed treatment of important industries.

Derr, "Photography for Students of Physics and Chemistry." Treats of the general principles and processes of photography.

Greene, "Coal and Coal Mines." An account of personal experiences.

Martin, "Story of a Piece of Coal." Condensed.

Meade, "Story of Gold." Non-technical.

Smith, "Story of Iron." Non-technical.

Snyder, "Chemistry of Plant and Animal Life." Popular.

Surface, "The Story of Iron." Non-technical.

Tower, "Story of Oil." A non-technical account of the industry.

Woolman and McGowan, "Textiles." A comprehensive account of the chemical nature of textiles.

HOUSEHOLD CHEMISTRY[1]

The home is the center of our national life. Chemistry plays a large part in the activities of the home, and some knowledge of chemistry is essential for its successful management.

ECONOMY IN THE HOME

Let us begin with the household itself. The United States Government recently issued a series of bulletins containing indispensable information on household chemistry and allied subjects (*Circulars* **55**, **70**, and **75**, Bureau of Standards, Washington, D. C.). The first tells about measurements in the home. The second describes the most common materials, other than food and drugs, used in the home. The third discusses the problem of safety. However, the main task in the home is to feed the family. You may find out how to do it in Rose's "Feeding the Family" (Macmillan, 1917; 449 pp.). The author tells in a clear and concise way how to provide proper food for different members of the family, young, old, thin, fat, sick, and well. Even if you yourself do not have to feed a family, you will find the book an entertaining and accurate account of the application of the science of nutrition to daily living. Household management is also a task in the home. A suggestive, practical book is Kinne and Cooley's "Foods and Household Management" (Macmillan, 1914; 401 pp.). This book treats of kitchen furnishings, preparation of food, cost and purchase of food, menus and dietaries, the family budget, how to buy, clean, and launder. Cook books are not usually regarded as books to read, but perhaps a cook book may be needed to supplement the two books just described. Farmer's "Boston Cooking-School Cook Book" (Little, Brown and Co., Boston, 1918; 656 pp.) is said to be "The best general cook book on the market." It contains considerable information about food besides the recipes. More description and fewer recipes will be found in Wellman's "Food Study" (Little, Brown and Co., Boston; 324 pp.); besides the selected recipes and the accurate descriptive material, there are practical tables of food values; a supplementary pamphlet on "Economy in Food" (36 pp.) contains helpful suggestions about saving money in buying, serving, storing, and cooking food.

FOOD AND NUTRITION

If you wish to read about the whole field of food and nutrition in its intimate relation to yourself and others, you will find reliable information in "Food and the War" (Houghton Mifflin Co., 1918; 379 pp.). Don't be misled by the title. Although this book was prepared under the direction of the United States Food Administration as a war book, it has become a peace book. It is full of all kinds of up-to-date information about food, nutrition, and diet. Incidentally, you will find in this book a great deal about feeding the Belgians and other European peoples. After all, eating is the large problem. We have many old-fashioned notions on food and eating. Now if you wish to start on the right track in improving your food habits, read Hawk's "What We Eat" (Harper, 1919; 232 pp.). This book is based on simple experiments which were performed to find out "what the human stomach actually thinks of all the common foods which enter into the diet of man." It answers in a simple way questions about drinking water with meals, drinking milk, coffee, and tea, oleomargarine versus butter, and eating ice cream, pastry, and candy. Parents who wish to feed their children properly ought to read this book. Sherman's "Chemistry of Food and Nutrition" (Macmillan, 1918; 454 pp.) is a more scientific book on food requirements and nutrition. While it is a textbook and perhaps intended for those who have some knowledge of chemistry, much of the book is suited to the needs of readers who wish to have reliable information about digestion, metabolism, food requirements, dietary standards, and inorganic food material. Special emphasis is laid on the food requirements of man. The best of the brief books on food values is Sy's "Food Values" (Bulletin No. 2, University of Buffalo, Buffalo, N. Y., 1917; 40 pp.; not available for free distribution). This compact account of the value of food is illustrated by colored charts depicting the proportions of the food principles in common foods.

If you desire general information about food products, read Bailey's "Source, Chemistry, and Use of Food Products" (Blakiston, 1917; 539 pp.). The book contains practical rather than specialized information about the sources, history, manufacture, preparation, composition, and uses of the important foods and beverages. One of the simpler books dealing with food, its nutritive value, and cost, is Olsen's "Pure Foods" (Ginn and Co., 1911; 210 pp.). Numerous experiments of varying degrees of difficulty are grouped at the ends of the chapters.

DEFEAT FOR THE HIGH COST OF LIVING

The relation of the composition of food to its cost may be found in two books. In Rose's "Laboratory Handbook for Dietetics" (Macmillan, 1917) there is an explanation of the problems involved in calculating food values, food requirements, and the construction of dietaries; while in Gephart and Lusk's "Analysis and Cost of Ready-to-Serve Foods" (American Medical Association, Chicago, 1915; 71 pp.) you will find both text and tables showing the composition, fuel value, and cost of well-known kinds of food served in a chain of New York restaurants. This is a unique book, because it shows the close relation of money to food actually prepared and served to thousands of patrons.

A book devoted entirely to household chemistry is Snell's "Elementary Household Chemistry" (Macmillan, 1914; 307 pp.). It contains text and experiments. The first half is devoted to general chemistry; the second half to household chemistry, including the study of foods, soap, bleaching, dyeing, and many other chemical topics.

Besides the books described in this reading course, there are many others you may wish to read. The following might be mentioned:

Belcher, "Clean Milk" (Orange Judd Co., N. Y.). Describes practical methods for excluding bacteria from milk.

Conn, "Bacteria, Yeasts, and Molds in the Home." Well-tested book on the relation of microörganisms to household affairs.

Grant, "Chemistry of Bread-Making." Treats of the process on a large scale.

Hart, "Leavening Agents." Brief discussion of baking powders and yeast.

Halligan, "Fundamentals of Agriculture." Answers many questions about the farm.

Jordan, "Principles of Human Nutrition." Non-technical; helpful tables.

Kellogg and Taylor, "The Food Problem." A war book on food and digestion.

Sherman, "Food Products." A comprehensive book (594 pages); contains an appendix on the Food and Drugs Act.

Vulté and Venderbilt, "Food Industries." Covers the production and manufacture of staple foods.

Wood, "Story of a Loaf of Bread." Starts with wheat growing and ends with the finished loaf.

GENERAL AND PHYSICAL CHEMISTRY[1]

The Great War raised American chemistry to its rightful place. First came the shutting-off of imports, then the demands of the Allies, and finally the needs of Uncle Sam in action. The story is so recent that, for the most part, it has yet to be told, but all men know that the American chemist acquitted himself well, both in research and in engineering. Is he quitting his efforts with the ending of the emergency? Of course not! Stimulated by great opportunities and by the knowledge that the nation now realizes much more clearly its need of him, the chemist returns to the arts of peace with a new spirit and with new recruits.

War called for quick action and the use of knowledge and skill already attained; now comes "the long pull," in which the successful will be those who best learn and keep up with their subject—who saturate themselves with it. And this means reading, both review and new.

UP OUT OF THE DARKNESS

To turn, once in a while, and look down over the way we have come is an inspiration; and what a fascinating past chemistry has! Our present-day commonplaces take on new interest when we reflect how they were once fought over. Moreover, yesterday's solution may contribute a hint to to-day's problem. "A History of Chemistry" by J. C. Brown (Blakiston, 1913; \$3.50[1]) is not only one of the latest of such histories, but is a valuable and eminently readable book. Those who are especially interested in recent progress (which, as is well known, has been very rapid) will find real enjoyment in reading "Chemical Discovery and Invention in the Twentieth Century" by W. A. Tilden (Dutton, 1917; \$3.50). It recounts the advances in pure and applied chemical science and describes several famous laboratories in different countries.

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[1] By Dr. Lyman C. Newell.

[1] By Dr. Austin M. Patterson.

"WHAT OTHERS HAVE DONE...."

One of the greatest stimuli one can have is acquaintance with the struggles and triumphs of great men through their biographies. "Famous Chemists" by E. Roberts (Macmillan; \$0.80) consists of short sketches of the life and work of such men as Boyle, Lavoisier, Liebig and Pasteur. A fascinating biography of Ramsay, the discoverer of the inert gases, has recently been written by an East Indian: "Sir William Ramsay," by T. C. Chaudhuri (Butterworth & Co., 1918; 66 pp.).

SOME AMERICAN ACHIEVEMENTS

American chemical history has been somewhat neglected by textbook writers, but Dr. Edgar F. Smith, chemist and also provost of the University of Pennsylvania, is a delightful writer and lecturer, and his fellow scientists are correspondingly indebted to him for two recent books about important early achievements here: "The Life of Robert Hare" (Lippincott, 1917; \$5.00) and "Chemistry in America" (Appleton, 1914; \$2.50).

FOR THE BEGINNER

Chemistry is one of the most fascinating of studies. The mysterious transformations which matter undergoes never fail to excite interest, which can be held if the subject is well presented. No one will be content with merely reading about chemical experiments or even with seeing them performed; he should *make them himself* to whatever extent is possible. Fortunately many elementary books are now available which contain directions for experiments or are accompanied by a laboratory manual. Laboratories are also numerous in these days, but the real future chemist will not be deterred by lack of access to one. Indeed, he will get some helpful experience in "rigging up" his own apparatus while finding his way to regular equipment. Among the best of the beginning books are "General Chemistry" by L. C. Newell (Heath, 1914; \$1.20, complete in two parts; or Part I, \$1.00, and Part II (experiments), \$0.60), which gives very full laboratory directions, and "A First Course in Chemistry" by McPherson and Henderson (Ginn; \$1.25), which is full of practical applications. Persons who have never studied chemistry but are mature enough to use a somewhat more advanced text may prefer "An Elementary Study of Chemistry" by McPherson and Henderson (Ginn, 1917; \$1.60).

COLLEGE COURSES

A well-known chemist once said that he made it a practice to read a good college chemistry every so often because, being immersed in his specialty, he could best realize the advance of the science in that way. There are many who could profit by doing this and who would enjoy the review. There are others who have already studied chemistry in an elementary way and are ready for something harder, or even beginners who are not afraid to tackle a college text. Among the books of proved value for these purposes are "General Chemistry for Colleges" by Alexander Smith (Century Co.; revised edition, 1916) and "A Textbook of Chemistry" by W. A. Noyes (Holt, 1913; \$2.25).

MORE INTERESTING THAN IT LOOKS

To some minds the words "theoretical chemistry" may not presage thrilling interest, yet after all man never observes facts that he does not immediately start to inventing theories about them. Even as a child he wants to know "why." Both facts and theory are indispensable to the growth of science and the aspiring chemist will lay a good theoretical foundation. "Elementary Chemical Theory" by J. M. Wadmore (Van Nostrand, 1912; \$1.50) is a simple treatment; a larger book, presupposing some knowledge of both physics and chemistry, is "Outlines of Theoretical Chemistry," by F. H. Getman (Wiley, 1913; \$3.50).

THE DAY OF PHYSICAL CHEMISTRY

Physical chemistry is a development of the last generation, but it will play a large part in the new era, commensurate with its importance to-day. Physics and chemistry are at bottom one, and physical chemistry is not a mere borderland province, but a central area of immense strategic importance. An excellent book for a first course is "Practical Physical Chemistry" by F. W. Gray (Macmillan; \$1.25). Somewhat more advanced are "Theoretical and Physical Chemistry" by S. L. Bigelow (Century Co., 1912; \$3.00) and "An Introduction to the Principles of Physical Chemistry" by E. W. Washburn (McGraw-Hill, 1915; \$3.50). The latter brings the discoveries in radioactivity and atomic structure up to a recent date.

AND COLLOIDS!

It is a long time since Graham first distinguished between "colloids" and "crystalloids," yet colloid chemistry is one of the most active fields of physical chemistry. An unusually readable little book which gives a very comprehensive idea of the subject is "An Introduction to the Physics and Chemistry of Colloids" by Emil Hatschek (Blakiston; \$1.00). One of the most satisfactory books on colloids in English is "The Chemistry of Colloids, and Some Technical Applications" by W. W. Taylor (Longmans; \$2.00).

SOME OTHER BOOKS

Historical

T. P. Hilditch, "A Concise History of Chemistry." Van Nostrand, 1911; \$1.05. A brief sketch, valuable as an aid in reviewing the subject; not recommended as an introduction.

A. Ladenburg, "Lectures on the History of the Development of Chemistry since the Time of Lavoisier." Translation; Van Nostrand, 1900. An interesting lecture course published originally in 1869 and brought down nearly to the end of the century by added lectures.

E. von Meyer, "A History of Chemistry." Third English edition; Macmillan, 1906. Long a standard book on this subject.

E. Thorpe, "History of Chemistry." 2 vols., illustrated. Putnam, 1910; \$2.00.

Beginning Chemistry

R. P. Brownlee, and others, "The Chemistry of Common Things." Allyn & Bacon, 1914; \$1.50. Rather superficial and unsystematic but contains a great deal of information about applied chemistry; presented in an elementary way.

J. C. Hessler and A. L. Smith, "Essentials of Chemistry." Sanborn & Co., New York, 1912; \$1.25 (with manual, \$1.45). A revised edition of a good textbook of the "assemblage of facts" type.

L. Kahlenberg and E. B. Hart, "Chemistry and Its Relations to Daily Life." Macmillan, 1913; \$1.25. A helpful, practical book by experienced teachers.

Wilhelm Ostwald, "Conversations in Chemistry." Wiley, 1906; Part I, \$1.50; Part II, \$2.00. General chemistry in simple language in the form of conversations between teacher and pupil.

Alexander Smith, "A Textbook of Elementary Chemistry." Century Co.; \$1.25. A very valuable and interesting book by a well-known author. Not as simple as some elementary works.

M. S. H. Unger, "Review Questions and Problems in Chemistry." Ginn, \$0.50. A complete and satisfactory compilation useful for those who have finished a beginners' course.

Advanced General Chemistry

C. L. Bloxam, "Chemistry, Inorganic and Organic." Tenth edition; Blakiston, \$5.50. A standard reference book probably containing more information in one volume than any other in English. It has some faults common to descriptive books which have passed through many editions.

W. McPherson and W. E. Henderson, "A Course in General Chemistry." Ginn, 1913; \$2.25. A college text in which modern theory and descriptive material are well balanced.

Wilhelm Ostwald, "Outlines of General Chemistry." Translation; third edition, 1912; \$4.50. A well-known book by a leading German chemist, in which chemistry is treated especially from the standpoint of energetics, the atomic theory being avoided.

Laboratory Manuals

W. S. Hendrixson, "A Laboratory Manual of General Chemistry." Fourth edition; Grinnell, Iowa, 1918. An elementary book which will give a good understanding of the relation of qualitative analysis to general chemistry.

A. B. Lamb, "Laboratory Manual of General Chemistry." Harvard Press, 1916. Contains advanced experiments, many of which are new, and is notable for its clear discussions. The last third of the book is devoted to inorganic preparations.

H. B. North, "Laboratory Experiments in General Chemistry." Van Nostrand, 1913; \$1.00. Contains 500 well-selected experiments.

Theoretical and Physical

S. Arrhenius, "Theories of Chemistry." Longmans, Green, 1907; \$1.75. A critical examination of chemical theories by a recognized authority.

S. Arrhenius, "Theories of Solutions." Yale Press, \$2.25. A course of lectures delivered in 1911 by a scientist of first rank and broad viewpoint. Valuable for those who are somewhat versed in physical chemistry.

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[1] Prices quoted throughout are as of the date of preparation of this report and are printed simply to serve as a guide to the general trend of prices.

W. H. Bragg and W. L. Bragg, "X-Rays and Crystal Structures." Macmillan, 1915; $2.25.

A. Findlay, "Osmotic Pressure." Longmans, Green, 1913; $1.00. An excellent exposition of a subject, the literature on which is somewhat confused.

A. Findlay, "Practical Physical Chemistry." Third edition; Longmans, Green, $1.20. A standard laboratory manual.

A. Findlay, "The Phase Rule and Its Applications." Longmans, Green, 1917; $1.75. A book of recognized merit which first appeared in 1904.

J. B. Firth, "Practical Physical Chemistry." Van Nostrand, 1916; $1.00. A laboratory manual not differing greatly from other books of its kind, but of recent date and including some experiments on colloids.

W. McC. Lewis, "A System of Physical Chemistry." Longmans, Green, 1916; 2 vols., $2.50 each. Very good as an advanced text.

J. W. Mellor, "Chemical Statics and Dynamics." London, 1914; $2.00.

R. A. Millikan, "The Electron." Chicago Press, 1917; $1.50. Based on the work of the author and his students.

J. L. R. Morgan, "The Elements of Physical Chemistry." Fifth edition; Wiley, $3.00. A well-known book which is not now altogether up to date in general viewpoint.

W. Nernst, "Theoretical Chemistry." Macmillan, 15s.

Wilhelm Ostwald, "Fundamental Principles of Chemistry." Translation; Longmans, Green, 1909; $2.25. A clear, attractive presentation by a foremost German chemist.

Wolfgang Ostwald, "An Introduction to Theoretical and Applied Colloidal Chemistry." Translation; Wiley, 1917; $2.50. A broad survey of the whole subject, taken from lectures delivered in 1913–14.

S. E. Sheppard, "Photo-Chemistry." Longmans, Green, 1914; $3.50. A most excellent resumé containing a surprising amount of material. Not to be confused with works on photographic chemistry.

S. Smiles, "The Relations between Chemical Constitution and Some Physical Properties." Longmans, Green, 1910; 14s. A most valuable collection and review of otherwise scattered data.

James Walker, "Introduction to Physical Chemistry." Macmillan. A good non-mathematical treatment.

R. Zsigmondy, "Colloids and the Ultramicroscope." Translation; New York; $3.00. A well-known text.

MISCELLANEOUS

R. M. Bird, "Modern Science Reader." Macmillan, 1911. A collection of interesting articles on pure and applied chemistry for collateral reading.

M. L. Dolt, "Chemical French." Chemical Publishing Co., $3.00. A companion volume to "Chemical German."

J. W. Mellor, "Higher Mathematics for Students of Chemistry and Physics." Fourth edition; London, 1913; $4.50. Enlarged edition of a highly successful work showing how the calculus and other mathematics are applied to practical problems.

J. C. Olsen, editor, "Van Nostrand's Chemical Annual." 1918; $3.00. A handbook of useful data.

J. R Partington, "Higher Mathematics for Chemical Students." Methuen & Co., London, 1911; 3s. 6d. A valuable book for students who have had some mathematics but need help in applying it to their chemical problems.

F. C. Phillips, "Chemical German." Second edition; Chemical Publishing Co., $2.00. Includes exercises in chemical German, extracts from the writings of German authors, and a German-English vocabulary.

INORGANIC AND ANALYTICAL CHEMISTRY[1]

American chemists made a substantial contribution to winning the war. They now face a great opportunity and a great responsibility. Most laymen now have a greatly increased interest in chemical developments as an important factor in our future national life. It is up to the chemist. He must broaden his outlook; he must add to his mental equipment, however good. The science of chemistry makes rapid progress. To pause or be satisfied with one's present training is to lose ground.

Inorganic chemistry has made noteworthy advances during the past twenty-five years, among which may be mentioned the discovery of the inert gases and of the radioactive elements, the further investigation of the rare earths, and the study of the complex compounds of cobalt, platinum, and other metals. Industrial processes based on inorganic chemistry have been of great importance in a military way and will be even more so in times of peace. An unconventional, racily written "Introduction to Modern Inorganic Chemistry" (Longmans, Green, 1914; $1.30) is furnished by J. W. Mellor. The same author has written another stimulating book called "Modern Inorganic Chemistry" (Longmans, Green, 1912; $2.20), which is prized by teachers and as a small reference book.

AN UP-TO-DATE SURVEY

Any one who has had a year or more of chemistry and who wishes to take up the special study of the inorganic department of the science, as well as the chemist who wishes—and it is a splendid idea—to review the field, will find an excellent and up-to-date survey in Alexander Smith's "Introduction to Inorganic Chemistry" (third edition, rewritten; Century Co., 1917; $2.60). Another standard book suitable for those who have already had a good preparation in chemistry, and some calculus, is "A Textbook of Inorganic Chemistry" by A. F. Holleman (fifth English edition; Wiley, 1916; $2.20).

THE PHYSICO-CHEMICAL VIEWPOINT

Inorganic chemistry and physical chemistry are, of course, not two separate and mutually exclusive fields. The first is part of a classification based on the kind of substances with which it has to deal, while the second is a particular way of looking at all substances. The study of inorganic chemistry from the physico-chemical standpoint is most instructive. "Inorganic Chemistry" by H. P. Cady (McGraw-Hill, 1912; $2.50) comes well recommended for this purpose.

LINKING UP WITH INDUSTRY

It is not often that one finds a treatment combining pure science with industrial applications, yet such an arrangement is entirely rational, for the two go hand-in-hand. E. Molinari's "Treatise on General and Industrial Inorganic Chemistry" (Blakiston, 1912; $6.50) is a well-known Italian work translated into English. It is provided with many illustrations.

METALS AND NON-METALS

This list would not be complete without a mention of Roscoe and Schorlemmer's comprehensive "Treatise on Chemistry" (Macmillan, Vol. I, 1911; Non-metals, $5.00; Vol. II, 1913; Metals, $7.50), which serves as a small reference work and is good reading besides.

FOR BALLOONS—HELIUM

One of the latest illustrations of the close relation of pure and applied science is the use in balloons of helium, a gas which only yesterday was considered rare and which day before yesterday (or so it seems) was known only by its spectrum in the sun! "The Gases of the Atmosphere" by William Ramsay (Macmillan, 1915; $2.00) presents an account of the discovery of helium and the other gases of the same family.

UNRAVELING THE COMPLEX

Years ago Werner proposed a novel theory for explaining the complex inorganic compounds. Many orthodox chemists looked askance at him, but he and his pupils have calmly gone their way accumulating evidence till no one can afford not to know something about it. "New Ideas on Inorganic Chemistry" by A. Werner (Translation; Longmans, Green, 1911; $2.50) records the Wernerian theories.

THE PLACE OF ANALYSIS

It is true that the present-day tendency is away from the job of the routine analyst, a title formerly thought of as almost synonymous with "chemist." Nevertheless, chemistry, being an "exact science," is and always will be dependent on analytical methods. The intelligent use of existing methods and the development of improved ones call for qualities of a high order. A good introduction to qualitative analysis may be had through "Qualitative Chemical Analysis" by A. A. Noyes (Macmillan; $1.50); "The Elements of Qualitative Analysis" by W. A. Noyes and G. McP. Smith (Holt); or "Qualitative Analysis" by F. P. Treadwell (fourth edition; Wiley; $3.00).

AVOIDING "RULE-OF-THUMB" METHODS

The really good analyst must be resourceful and hence must have a good understanding of the principles on which analysis is based. A great advance in the presentation of these principles is made in "The Elements of Qualitative Analysis" by J. Stieglitz (Century Co., 1911; Vol. I, $1.40; Vol. II (laboratory manual), $1.20). A well-selected course presented throughout from the standpoint of electrolytic dissociation and mass action is Bailey and Cady's "A Laboratory Guide to the Study of Qualitative Analysis" (eighth edition; Blakiston; $1.50).

NOT ONLY "WHAT?" BUT "HOW MUCH?"

A leading biological chemist, who died recently, used to state that he wished that all specialists in his line had had the good old-fashioned drill in quantitative analysis. Certainly the training which it gives is valuable to any chemist. A selected course with a good introduction is given in the "Quantitative Analysis" of H. P. Talbot (Macmillan; $1.50). "Quantitative Chemical Analysis" by Clowes and Coleman (tenth edition; Blakiston, 1914; $3.50) is a carefully revised form of an excellent standard text, and J. C. Olsen's "Textbook of Quantitative Chemical Analysis" (fifth edition; Van Nostrand, 1916; $3.50) is also a standard work.

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[1] By Dr. Austin M. Patterson.

THE USE OF THE BLOW PIPE

In practiced hands this little instrument, familiar to every chemistry freshman, may be made to perform wonders, not only in qualitative analysis, but also for quantitative work. Its use is a real art, fascinating to those who specialize in it. Plattner's "Manual of Qualitative and Quantitative Analysis with the Blow Pipe" (Translation; eighth edition revised; New York, 1912; $4.00) is one of the best-known books on this subject. A small treatise of recent date is G. M. Butler's "Pocket Handbook of Blow Pipe Analysis" Chapman and Hall, 1916; $0.75).

SOME OTHER BOOKS

Inorganic Chemistry

P. E. Browning, "Introduction to the Rarer Elements." Third edition; Wiley, 1912; $1.50. The latest edition of a book of recognized value.

J. N. Friend, *et al.*, "A Textbook of Inorganic Chemistry." In nine vols.; Vol. I, Parts 1 and 2; Lippincott, $3.00. Part I is an introduction, and Part 2 treats of the inert gases. The beginning of what promises to be a standard reference work.

F. S. Kipping and W. H. Perkin, "Inorganic Chemistry." Part I (non-metals); Chambers, 1917; $2.00.

D. Mendeléeff, "The Principles of Chemistry." Third English edition; 2 vols.; Longmans, 1905; $10.00. This book by the famous Russian chemist was given its original form in 1868–70. It has become a classic and is still a fertile source of ideas for research.

L. C. Newell, "Laboratory Manual of Inorganic Chemistry for Colleges" Heath, 1909; $2.00. A book noted for its clear and full directions and the comparative simplicity of its apparatus.

Analytical Chemistry

W. C. Blasdale, "Principles of Quantitative Analysis." Van Nostrand, 1914; $2.50. A well-arranged introduction to quantitative analysis, with a good discussion of the "reasons why."

E. G. Mahin, "Quantitative Analysis." McGraw-Hill, 1914; $3.00. Combines the principles and standard methods with some industrial applications. Elaborate discussion is avoided.

(To be concluded in the August issue)

SCIENTIFIC SOCIETIES

IN THE ALEMBIC OF PUBLICITY

By John Walker Harrington

A. C. S News Service, New York, N. Y.

As a sign of what may be done to bring the progress of chemistry before the public at the fall meeting of the American Chemical Society, to be held in Chicago next September, stands the record of our publicity for the St. Louis sessions.

The notice which that 59th gathering received from the press was obtained, too, in days of a famine of paper and of a feast of general news.

That the volume of publicity was nearly twice that of the Philadelphia meeting indicates, however, that there is a constantly increasing interest in chemistry throughout the United States. This recognition was due entirely to chemistry itself, for unlike the conclave of the knights of the retort in the City of Brotherly Love, the meeting at St. Louis had as speakers no Cabinet members or men who were figures in national politics. The assemblage at St. Louis, therefore, probably furnished as thorough a test of the chemical appeal to the people as could be had.

As there has been time to organize the publicity of the Society in every direction, the A. C. S. News Service enlisted the enthusiastic coöperation of the Associated Press, the United Press, the International News Service, and other large news gathering organizations.

The distribution of advance material was made from three points. By consulting the accompanying map it will be seen that the newspapers interested are mostly within circles described with a 500 mile radius from the cities of New York, St. Louis and San Francisco. In the strip of territory stretching downward from North Dakota and including South Dakota and the western portions of Nebraska, Kansas, Oklahoma, and Texas, publications are far from numerous, and there are also comparatively few in eastern Montana and in New Mexico.

No state, however, could have failed to have been informed by the press concerning the activities of the American Chemical Society, as newspapers circulate far beyond the borders of the state in which they are published. At El Paso, for instance, close to the boundary line between Texas and New Mexico, are several important newspapers which circulate to the north and into a considerable territory of New Mexico. Many papers printed in the United States serve Canada, in which country also four of the leading journals carried reports of the St. Louis meeting.

On the map printed in this issue has been indicated by shaded areas the hundred mile radius of the circulation of the various newspapers, following a rule in vogue among newspaper publishers.

The publicity returns, as shown, are visualized according to their geographical as well as their journalistic trend.

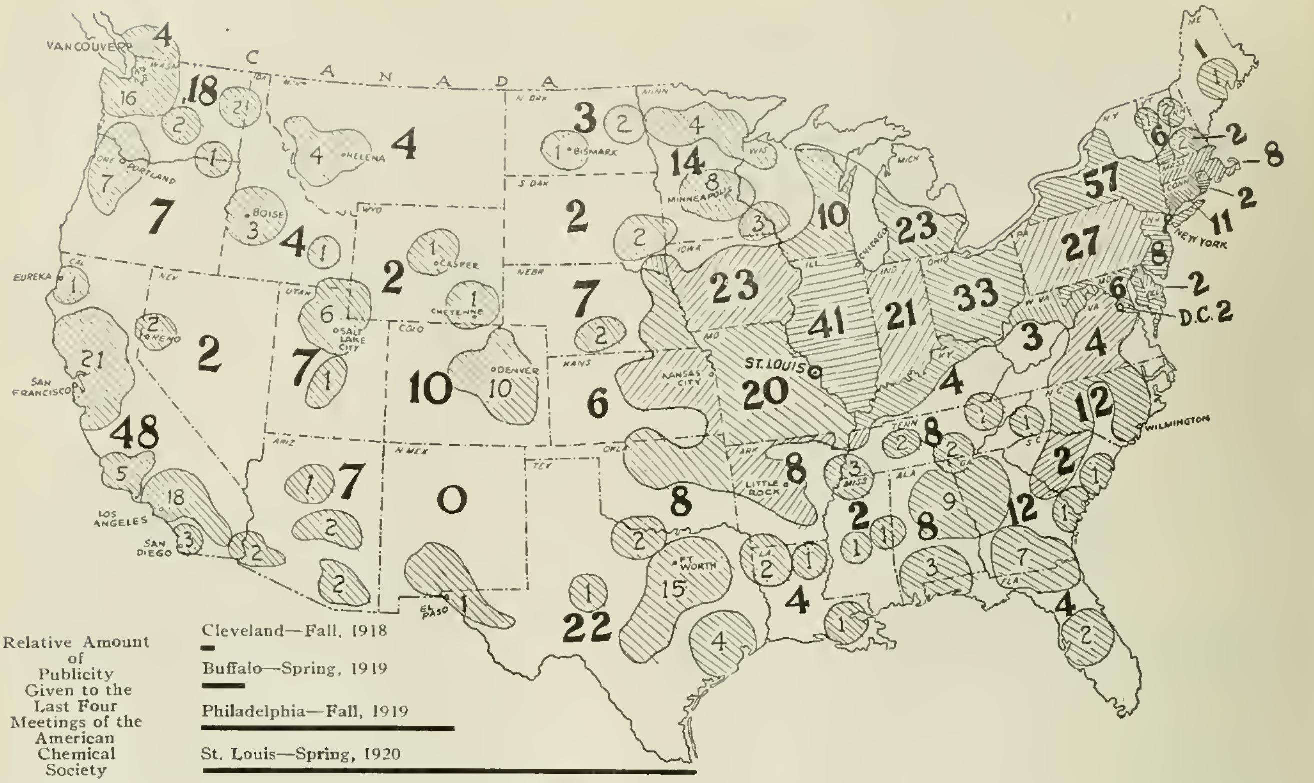
Even when the last returns from our four clipping agencies will have been obtained, only a fraction of the actual amount of publicity given will be recorded. Some publicity managers say that even with the vigilant eyes of several clipping organizations on the job, barely ten per cent of the articles actually printed can be shown by agencies; while others estimate from fifteen to twenty per cent. Taking the actual returns to date, however, as an index, the results may be considered as satisfactory.

There have been received (omitting duplicates) 1,180 press cuttings, measuring 8,460 inches, or 118,440 agate lines. From the Philadelphia meeting, which was the first meeting of the Society at which a nation-wide publicity program was installed, 700 press notices were collected. As far as can be learned, the meeting at Cleveland in the fall of 1918 was practically ignored by the papers of that city and received about 15 notices from the fourth estate. The spring meeting of 1919, held in Buffalo, received 67 notices in all from the Buffalo papers, and 35 from the press at large, as indicated by the reports of the clipping agencies. In the year 1919 there were distributed, exclusive of the two general meetings of the Society, 33 bulletins, which resulted in 894 clippings, measuring 7,963 inches. This shows the value of the news interest in disseminating chemical information, as the returns from St. Louis are larger than those from the bulletins issued for all of last year.

In the various states the press was influenced in the amount of space given to the St. Louis meeting to a large extent by the number of members of the Society in the respective commonwealths, as well as by the presence of chemical industries or of enterprises under chemical control.

New York, a state close to the chemical center of the United States, as shown by the membership of the Society, leads the accompanying list with 57 papers giving more or less full reports of the St. Louis meeting, while neighboring Pennsylvania, pioneer state of industrial chemistry, has 27. California, in which the already large chemical roster is rapidly increasing, is second, with 48 newspapers. From the main distributing center, St. Louis, which to quote the slogan of that enterprising city is "surrounded by the United States," the 500 mile radius has full play. Twenty leading newspapers in Missouri; 41 in Illinois; 33 in Ohio; 21 in Indiana; 14 in Minnesota; 10 in Wisconsin, and as many in Arkansas, evinced a lively interest in the proceedings of the Society. In this connection, the A. C. S. News Service wishes to acknowledge the able assistance of the St. Louis Convention and Publicity Bureau, the coöperation of which was obtained by the Local Section.

In every state, with the exception of New Mexico, in which there is no section of the Society and where manufacturing chemistry has not as yet made a place, the papers had accounts of the St. Louis meeting. A list of the states, prepared in


Relative Amount of Publicity Given to the Last Four Meetings of the American Chemical Society

accordance with their quotas of the 545 newspapers which are known to have reported the spring meeting of 1920, is submitted for consideration.

Number of Newspapers in Each State Which Printed Reports of the St. Louis Meeting of The American Chemical Society[1]

	Newspapers		Newspapers
New York	57	Oregon	7
California	48	Utah	7
Illinois	41	Kansas	6
Ohio	33	Maryland	6
Pennsylvania	27	Vermont	6
Iowa	23	Florida	4
Michigan	23	Idaho	4
Texas	22	Kentucky	4
Indiana	21	Louisiana	4
Missouri	20	Montana	4
Washington	18	Virginia	4
Minnesota	14	North Dakota	3
Georgia	12	West Virginia	3
North Carolina	12	Delaware	2
Connecticut	11	District of Columbia	2
Colorado	10	Mississippi	2
Wisconsin	10	Nevada	2
Arkansas	8	New Hampshire	2
Alabama	8	Rhode Island	2
Massachusetts	8	South Carolina	2
New Jersey	8	South Dakota	2
Oklahoma	8	Wyoming	2
Tennessee	8	Maine	1
Arizona	7	New Mexico	0
Nebraska	7	Total	545

[1] These reports, based on the returns of 4 clipping agencies, necessarily represent only a fraction of the publicity obtained. The common rule would be to multiply these results by 7 to estimate the volume of publicity.

There is food for thought in the character of the subjects which received the most attention from the lay press, as shown by an analysis of clippings received.

Probably the last thing in the world in which a newspaper editor might be considered as having an interest several years ago would be a "colloid." The greatest number of clippings, however, came from Mr. Jerome Alexander's paper, "Some Practical Applications of Colloid Chemistry." The description of the colloidal fuel evolved by Lindon W. Bates was the cause of the wide popular interest evinced in what ordinarily would have seemed an abstraction.

The papers of the new Leather Section, bearing as they did upon the all-important subject of shoes, were also favored at the copy desks. The proceedings of the Rubber Section, especially the paper on "The Microscopic Examination of Rubber Products," by Dr. H. J. Masson and Miss Irene Diner, bounded and rebounded through the press because they had a bearing on the durability of rubber tires. The editors know that every American, in fact or thought, is an automobile owner. The potash papers of Dr. Turrentine, concerning American agriculture, and also two papers which indicated the making of dyes from the humble corn cob, were likewise favorites.

A brief interview obtained from Dr. Ralph H. McKee, in which he spoke of the use of cheap alcohol for automobile fuel, was reprinted in scores of papers throughout the United States, and stood fourth in popularity.

One factor in the success of the St. Louis publicity was the coöperation of various members of the Society, who at the request of the technical manager gave time to explain details to inquiring newspaper representatives, and to assist in the preparations of such bulletins as had to be issued from the press room at the last minute.

The results obtained in publicity work for the Society, by the way, depend largely upon the issuing of abstracts and news synopses of papers well in advance of meetings, and subject to release. In this way, with the coöperation of the press associations, matter can be distributed over the United States and put in type, ready for printing at the touch of the telegrapher's keys. The A. C. S. News Service, in preparing for the Chicago meeting, would, therefore, appreciate the prompt forwarding of abstracts or condensations of technical papers, so that in September it may stand ready to serve the American press.

CONVENTION OF CANADIAN CHEMISTS

The convention of Canadian Chemists, held at Toronto on May 27 and 28, 1920, was a great step towards the consolidation of chemical interests in Canada for purposes most beneficial to the welfare of the profession, the industries they represent, and the country as a whole.

For those not perfectly familiar with the rapid developments among chemical organizations in Canada in recent years, it may be news that there are two quite active groups of organized chemists in the Dominion. The Society of Chemical Industry

Photo by British and Colonial Press, Toronto

Left to Right, Front Row: L. J Rogers, Lash Miller, W. L. Goodwin, R. F. Ruttan, W. H. Ellis, Chas. H. Herty, H. van der Linde, T. H Wardleworth. Second Row: H. E. Bigelow, J. T. Burt-Gerrans, A. Lehman, F. T. Shutt, G. D MacIntyre, H. J. Roast, J. B. Bell, A. R. McLean, H. M. Lairash. Third Row: L. E. Westman, F. C. Collier, G. A. Evans, L. F. Goodwin. Back Row: F. J. Hambly, H. M. Lancaster, W. H. Thom C. F. Thurlow, Alfred Burton, L. T. Acton, E. G. R. Ardagh, J. Watson Bain, S. J. Cook

has had a Canadian Section for eighteen years. Branches have been established in Toronto, Montreal. and Ottawa, and a Canadian Pacific Section established in Vancouver to develop western interests. In Manitoba, the Manitoba Chemical Society, centered in Winnipeg, attends to the chemical interests of that province, while the eastern provinces of New Brunswick and Nova Scotia have organized under the Maritime Chemists' Association. All these bodies are broad in their interests and aim to include in their membership all those who are interested in chemistry.

The Canadian Institute of Chemistry is a dominion-wide organization of chemists, restricted to those whose academic or industrial training has been sufficient to qualify them as fully trained and competent professional men. The recent gathering was a joint meeting of these several organizations.

The University of. Toronto offered rather ideal facilities to the visiting chemists. Space for an industrial exhibit was secured in the Mining Building for some twelve companies whose displays went to show that the idea of such an exhibition of apparatus and chemicals had a strong appeal to the representatives of manufacturers and laboratories who were present. This will probably become a growing feature of future conventions. The favor of using Hart House, which is the latest addition to the buildings of the University, and in many ways one of the most remarkable and beautiful buildings on the continent devoted to the use of university students and professors, was fully appreciated. The meetings held there were most impressive and perhaps revealed best the spirit of the convention.

The message of Dr. Chas. H. Herty, who was the honored guest of the chemists of Canada, was delivered here. The problems of "Chemistry under a Constitutional Government" are alike both in the United States and Canada, and for that matter throughout the Anglo-Saxon world. A resumé of what was being done by a proper utilization of the public press of the United States in matters relating to the building up of a national series of chemical industries, free from harmful connections and with the exalted aim that the proper function of industrial chemistry was to facilitate happiness and peace, and not to promote destruction and war, was an ideal which voiced fully the sentiments of every Canadian chemist.

The Canadian Institute of Chemistry, under the guidance of Professor J. W. Bain, president, and H. J. Roast, secretary, reported a successful year. The membership has grown rapidly and a permanent constitution is being developed. The great distances separating members makes the working out of details in such an organization a slow process, but the end in view, namely, a Canadian national chemical organization, designed to represent the chemists of the Dominion in matters relating to both internal and external affairs, is something much to be desired and sure to receive support.

TORONTO, CANADA L. E. WESTMAN

REPORT OF THE COMMITTEE ON COTTONSEED PRODUCTS, DIVISION OF INDUSTRIAL AND ENGINEERING CHEMISTRY, AMERICAN CHEMICAL SOCIETY[1]

This report covers cottonseed, cottonseed oils, cake and meal, crude cottonseed oil, crude peanut oil, crude coconut oil, crude soy-bean oil, refined oils, soap stock and acidulated soap stock, titer tests, and an appendix specifying oil grades, both crude and refined. It has received the unanimous endorsement of the committee: Thomas C. Law, *Chairman*, Frank N. Smalley, Archibald Campbell.

I—COTTONSEED

1—The sample to be used should weigh not less than 10 g. (approximately 100 seed).

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[1] Approved by the Supervisory Committee on Standard Methods of Analysis, American Chemical Society.

2—Cut the seed by hand, using a sharp knife or similar instrument; remove the kernels and determine the percentage of the kernels and the hulls by weight.

3—Determine the percentage of moisture in the hulls.

4—Determine the percentage of moisture, oil, and nitrogen in the kernels.

(*a*) Determine moisture and nitrogen strictly in accordance with the methods given below under Meal.

(*b*) Determine the percentage of oil in the same manner as given below for Meal, but extract the sample for 2 hrs., then regrind it and extract again for 2 hrs. Remove the last trace of petroleum ether by heating the flask over a flame until the contents just begin to smoke.

5—Calculate moisture, oil, and ammonia in the whole seed.

6—Determine the yield of meal by multiplying the percentage of ammonia in the whole seed by 1900 and divide by the percentage of ammonia desired in the meal, expressing the results thus obtained in "Available pounds of meal per ton of seed."

7—Determine the yield of oil by multiplying the percentage of oil in the whole seed by 1900 and divide by 7.5, the result being total gallons. Deduct 60 lbs. or 8 gal. to allow for loss in milling and express the results as "Available gallons of oil per ton of seed."

8—In the case of damaged seed make an additional deduction in allowing for the milling loss on a basis of one additional gallon for each 10 per cent damaged from 5 to 25 per cent and an additional gallon for each 5 per cent of damaged seed above 25 per cent.

Air-tight friction-top tin containers must be used for forwarding samples of cottonseed.

II—COTTONSEED HULLS

1. WHOLE SEED AND UNCUT MEATS—Pick out the whole seed and uncut meats in 100 g. of the sample and report the percentages determined by weight.

2. OIL—Place 5 g. of the hulls, free from meats and seeds, in a suitable extraction apparatus and extract for 3 hrs. with petroleum ether, boiling below 65° C. Evaporate the extract at the temperature of boiling water to constant weight and report as percentage of oil.

3. FORM OF REPORT—The following form of report is recommended as the standard, employing the following conversion factors:

(*a*) To convert whole seed to oil, use the factor 0.2.

(*b*) To convert uncut meats to oil, use the factor 0.33.

Oil in whole seed and uncut meats, per cent.
Oil in hulls, per cent.
Total oil in hulls, per cent.

4. LINT DETERMINATION—Dry 5 g. of hulls, free from meats and seed, to constant weight in a moisture dish. Transfer to a beaker containing 40 cc. of sulfuric acid (sp. gr. 1.84), and stir with a glass rod for exactly 30 sec. Pour immediately into a beaker containing 200 cc. of water and wash all particles of hulls from the acid beaker with an additional 50 cc. of water. Filter at once through linen cloth, using suction. Thoroughly washed tracing cloth, placed in a hard rubber straining funnel, is recommended for this purpose. Wash until free from acid, drain the residue thoroughly and transfer to the original moisture dish. Dry at 110° C. to constant weight. Three determinations should be made and the average of those agreeing within 1 per cent reported. Calculate the percentage of lint on the original moisture and report as available hull fiber or lint. The average cellulose content of hull fiber is 70 per cent, which factor takes into consideration the solvent action of the acid on hulls.

III—CAKE AND MEAL

1. PREPARATION OF SAMPLE—Grind the sample to uniform fineness and then mix thoroughly, but without sieving. These operations must be performed as rapidly as possible to avoid loss or gain of moisture.

2. MOISTURE—Heat from 2 to 5 g. of the sample for 3 hrs. in an oven at a temperature of 100° C., using an aluminum dish with cover. As soon as the dish is removed from the oven, cover, and cool in a desiccator. Report the loss in weight as moisture. For comparative purposes moisture tests are required on all analytical reports.

3. OIL—Extract 2 to 5 g. of the sample for 3 hrs. in any suitable fat extraction apparatus, using petroleum ether, boiling below 65° C., as the solvent. Evaporate off the ether until no trace remains. Weigh the residue and report it as oil.

4. FAT—Whenever cottonseed meal is sold as a feedstuff a sample must be analyzed for fat according to the official method of the Association of Official Agricultural Chemists.

5. NITROGEN—AMMONIA—PROTEIN—(*a*) Digest 1.7034 g. of the sample with approximately 0.5 g. of metallic mercury or 0.7 g. of mercuric oxide, 10 g. of sodium or potassium sulfate, and 25 cc. of sulfuric acid (sp. gr. 1.84). Place the flask in an inclined position and heat below the boiling point of the acid from 5 to 15 min., or until frothing has ceased. Now increase the temperature and continue digestion until the liquid becomes colorless or until complete digestion has been obtained. From this point on employ the regular Kjeldahl method except that no potassium permanganate is to be added.

(*b*) DISTILLATION—After cooling the digestion flask and contents, add about 300 cc. of distilled water, a few pieces of zinc to prevent bumping, and 25 cc. of a 4 per cent solution of potassium or sodium sulfide, or a sufficient amount to precipitate all the mercury. After mixing thoroughly, add 60 cc. of a caustic soda solution, sp. gr. 1.50, or sufficient to make the solution strongly alkaline, pouring it down the side of the flask, so that it does not mix at once with the acid solution. Connect the flask with a condenser of block tin, mix the contents of the flask by shaking, and distil into an accurately measured quantity of standard sulfuric acid solution, preferably 0.5 *N*, to which have been added 50 cc. of distilled water. Continue the distillation until at least 200 cc. of distillate are obtained, taking care that the delivery tube reaches below the level of the standard acid. Now titrate the distillate with a standard fixed alkali solution, preferably 0.25 *N* sodium hydroxide.

(*c*) A blank should be run on all the agents employed.

(*d*) The conversion factor used is nitrogen × 6.25 = protein. The atomic weights used are nitrogen 14.01, and hydrogen 1.008.

IV—CRUDE COTTONSEED OIL[1]

1. SHAKING THE SAMPLE—Samples submitted for analysis must be thoroughly shaken with the container in an inverted position before drawing a portion for analysis.

2. MOISTURE OR VOLATILE MATTER—Place 10 g. of the well-mixed sample in a tared metal or porcelain dish and heat over a direct flame with a rotating and rocking motion until the oil barely smokes. Cool and report the loss in weight as moisture. Set aside the residue for meal determination.

3. MEAL OR IMPURITIES—Wash the residue from the moisture determination into a beaker, using kerosene, and warm to dissolve the oil. Now filter on a tared Gooch crucible and wash the residue with petroleum ether until free from oil, dry to constant weight, divide by 0.8, and report as percentage of meal or impurities.

4. FREE FATTY ACIDS—Weigh or measure with a pipette 7.05 g. of the well-mixed oil sample into a 4-oz. oil bottle. Add 50 cc. of neutral saturated, chemically pure sodium chloride solution and 2 cc. of phenolphthalein indicator. Titrate with standard 0.25 *N* sodium hydroxide solution until, upon the addition of one drop and violent shaking, a permanent pink color results. Report as percentage of free fatty acid. The reading of the burette in cubic centimeters is the percentage of free fatty acid calculated as oleic acid. (A free fatty acid determination is required on all oils.)

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[1] See appendix for definition of grades.

5. REFINING LOSS—(A) *Prime Oil*—(*a*) The quantity of dry sodium hydroxide to be used in refining prime oil must not exceed 1.097 per cent by weight of the oil for hydraulic pressed oils, or 1.437 per cent by weight of the oil for cold pressed oils, and must be employed in solutions of 10, 12, 14, 16, 18, and 20° Baumé at 20° C. No oil shall be rejected unless treated with three or more sodium hydroxide solutions of the above strengths; nor shall any claim for excessive refining loss be established if it can be proven that the color can be made with a smaller loss than is produced with the maximum amount of sodium hydroxide allowed; nor shall any claim for deficiency in color be established if it can be proved that the color can be obtained without exceeding 9 per cent refining loss with the maximum amount of sodium hydroxide allowed.

(*b*) APPARATUS—*Scales*, of 1,000 g. capacity and sensitive to 0.5 g.

Weights, 500 g. to 0.5 g.

Refining cups, seamless or enameled cups 4.5 in. in diameter and 4 in. in depth.

Refining apparatus, a mechanical stirrer the speed of which may be controlled. Water bath fitted with thermometer and suitably arranged to hold cups used in the tests.

(*c*) REAGENTS—Sodium hydroxide solutions of 10, 12, 14, 16, 18, and 20° Baumé at 20° C., made from a saturated solution of pure material, containing 77.5 per cent sodium oxide.

SODIUM HYDROXIDE TABLE

Degrees Baumé	NaOH Contents Per cent	Amount Per cent
10	6.55	16.8
12	8.00	13.7
14	9.42	11.6
16	10.97	10.0
18	12.62	8.7
20	14.37	7.6

(*d*) REFINING PROCESS—Place 500 g. of a thoroughly mixed sample of crude oil in a tared refining cup and bring it to a temperature of from 24° to 27° C. Add the necessary amount of sodium hydroxide solution and stir for at least 5 min. without heating, and in the case of cold pressed oil, not less than 30 min. Apply heat and raise the temperature gradually until at the end of 15 min. a temperature of 40° C. has been reached. Stir constantly and continue stirring until a complete separation of the oil and soap stock results. At times, to effect this separation, it will be necessary to attain a temperature of 65° C. When a separation has been secured, place the cup in a water bath at 45° C. for 3 hrs. Allow the cup to stand overnight or cool thoroughly, so that the soap stock will become hard and firm. Now decant the refined oil into a tared refining cup and drain the soap stock for 20 min. If necessary, melt the soap stock on the steam bath, to complete the separation of the oil. Weigh both oil and soap stock cups and contents.

(*e*) CALCULATIONS—The refined loss should be determined by two methods of calculations, the results of which should check within 0.25 per cent.

Method 1—Weight of crude oil minus the weight of refined oil.

Method 2—Weight of soap stock, plus loss in evaporation, minus the weight of sodium hydroxide solution used.

(B) *Off Oil*—(*a*) Any oil with less than 3 per cent of free fatty acid may be refined with any amount of sodium hydroxide solution necessary to neutralize the free fatty acid plus a reasonable excess, provided that the total sodium hydroxide does not exceed 1.097 per cent of the oil for hydraulic pressed oils, or 1.437 per cent for cold pressed oils. On any oil with over 3 per cent free fatty acid three refinings shall be made, using different strengths of sodium hydroxide solution, provided that the maximum amount of sodium hydroxide allowed in the table below is not exceeded, and that one of the tests be made with this maximum amount.

(*b*) APPARATUS—The same as noted under Prime Oil.

(*c*) REAGENTS—Sodium hydroxide solutions of 10, 12, 14, 16, 18, 20, 22, and 24° Baumé at 20° C. made from a saturated solution of the pure material (77.5 per cent sodium oxide).

(*d*) SODIUM HYDROXIDE TABLE FOR USE ON OFF OILS

Weight of Caustic Necessary to Neutralize Free Fatty Acids
Plus 0.6716 Per cent Excess NaOH

Free Fatty Acids	NaOH	Excess	Degrees Baumé 10	12	14	16	18	20	22	24
3.0	0.4245	1.0970	16.8	13.7	11.5	10.0	8.7	..	..	..
3.5	0.4963	1.1679	17.8	14.6	12.4	10.7	9.3	..	..	..
4.0	0.5672	1.2388	18.9	15.5	13.1	11.3	9.8	..	..	..
4.5	0.6381	1.3097	..	16.4	13.9	11.9	10.4	9.1	..	..
5.0	0.7090	1.3806	..	17.3	14.7	12.6	10.9	9.6	..	..
Plus 0.7500 Per cent Excess NaOH										
5.5	0.7799	1.5299	..	19.1	16.2	13.9	12.1	10.6	..	..
6.0	0.8508	1.6008	..	20.0	17.0	14 6	12.7	11.1	..	..
6.5	0.9217	1.6717	..	..	17.8	15.2	13.2	11.6	..	..
7.0	0.9926	1.7426	..	..	18.5	15.9	13.8	12.1	..	..
7.5	1.0635	1.8135	..	..	19.2	16.5	14.3	12.6	..	..
Plus 0.8750 Per cent Excess NaOH										
8.0	1.1344	2.0094	..	..	21.3	18.2	15.8	13.9	..	..
8.5	1.2053	2.0803	..	..	22.1	19.0	16.5	14.5	..	..
9.0	1.2762	2.1512	..	..	22.8	19.6	17.0	15.0	..	..
9.5	1.3471	2.2221	..	..	23.6	20 3	17.6	15.5	..	..
10.0	1.4180	2.2930	..	..	24.3	20.9	18.1	16.0	..	..
Plus 1.0 Per cent Excess NaOH										
10.5	1.4889	2.4889	..	..	..	22.7	19.7	17.3	15.6	14.1
11.0	1.5598	2.5598	..	..	..	23.3	20.3	17.8	16.1	14.5
11.5	1.6307	2.6307	..	..	..	24.0	20.9	18.3	16.5	14.9
12.0	1.7016	2.7016	..	..	..	24.6	21.4	18.8	17.0	15.3
12.5	1.7725	2.7725	..	..	..	25.3	22.0	19.3	17.4	15.7
Plus 1.125 Per cent Excess NaOH										
13.0	1.8434	2.9684	..	..	..	27.0	23.5	20.6	18.6	16.8
13.5	1.9143	3.0393	..	..	..	27.7	24.1	21.1	19.1	17.2
14.0	1.9852	3.1102	..	..	..	28.4	24.7	21.7	19.5	17.6
14.5	2.0561	3.1811	..	..	..	29.0	25.2	22.1	20.0	18.0
15.0	2.1270	3.2520	..	..	..	29.7	25.8	22.6	20.4	18.4
Plus 1.25 Per cent Excess NaOH										
15.5	2.1979	3.4479	..	..	..	31.4	27.3	24.0	21.7	19.5
16.0	2.2688	3.5188	..	..	..	32.1	27.9	24.5	22.1	19.9
16.5	2.3399	3.5899	..	..	..	32.7	28.4	25.0	22.5	20.3
17.0	2.4106	3.6606	..	..	..	33.4	29.0	25.5	23.0	20.7
17.5	2.4815	3.7315	..	..	..	34.0	29.6	26.0	23.5	21.1
Plus 1.375 Per cent Excess NaOH										
18.0	2.5524	3.9274	..	..	..	35.8	31.1	27.3	24.7	22.3
18.5	2.6233	3.9983	..	..	..	36.4	31.7	27.8	25.1	22.6
19.0	2.6942	4.0692	..	..	..	37.1	32.3	28.3	25.6	23.0
19.5	2.7651	4.1401	..	..	..	37.8	32.8	28.8	26.0	23.5
20.0	2.8360	4.2110	..	..	..	38.4	33.4	29.3	26.5	23.9

(*e*) REFINING PROCESS—The same method is used as in the case of Prime Oil, with the following variations: After adding the sodium hydroxide solution, stirring is continued for 15 min. without heating; then the oil is heated to 60° C., which temperature is to be reached during an interval of 15 min., and a maximum temperature of 65° C. is allowed.

6. COLOR—(*a*) The color of refined oil is to be reported in terms of Lovibond's equivalent color scale, using yellow and red glasses.

(*b*) The color scale examinations shall be made as follows: Place the oil in a white polished-bottom bottle or cylinder of such depth that a column of oil of 5.25 in. can be accurately measured therein. Such a bottle or cylinder is to be not less than 0.75 in. in internal diameter. The bottle shall be placed in a tintometer which is to be protected from any light except reflected white light, and the reading made at a temperature of 21° C. or by such method as may be recommended by the U. S. Bureau of Standards, provided the same be approved by the Cottonseed Products Committee of the AMERICAN CHEMICAL SOCIETY and provided that the color determined shall be expressed in Lovibond terms. If the oil is of a deeper color than the glass standard 35 yellow, 7.6 red, it shall not be classed as prime.

7. FLAVOR—Oil which is not rancid, musty or sour, and does not have a flavor foreign to cottonseed oil, shall be graded as prime flavor.

V—CRUDE PEANUT OIL

1. REFINING PROCESS—The method of refining shall follow the same general procedure as in the case of Crude Cottonseed Oil (p. 708); but in all cases the stirring shall be continued at least 30 min. before applying heat; and when the free fatty acid does not exceed 3 per cent, one test shall be made using 10° Baumé

sodium hydroxide solution with 0.1 per cent sodium hydroxide in excess of the amount necessary to neutralize the free fatty acids.

VI—CRUDE COCONUT OIL

1. REFINING PROCESS—Follow the same general procedure as in the case of Crude Cottonseed Oil. In the case of oils containing less than 5 per cent free fatty acids the amount of sodium hydroxide used shall not be more than 0.2 per cent in excess of the amount necessary to neutralize the free fatty acids.

VII—CRUDE SOY-BEAN OIL

1. REFINING PROCESS—Follow the same general method as in the case of Crude Cottonseed Oil. In the case of oils containing less than 3 per cent free fatty acids the amount of sodium hydroxide used shall not be more than 0.2 per cent sodium hydroxide in excess of the amount necessary to neutralize the free fatty acids.

VIII—REFINED OILS

1. BLEACHING—Place 300 g. of refined oil in a refining cup, heat to 120° C. and add 6 per cent of standard fuller's earth. Stir thoroughly for 5 min., taking care that the temperature does not fall below 105° C. Filter through filter paper and after sufficient oil has passed the filter to insure clearness, collect a sample for color reading. Cool to 21° C. and determine the color reading on a column 5.25 in. in depth, according to the method under IV, *6a*.

2. COLD TEST—(Applicable to winter oils.) Fill a 4-oz. sample bottle with the oil to be tested, insert a thermometer, and seal hermetically. Warm the oil slowly to a temperature of 26° C. and allow it to remain for 15 min. Chill and hold at a temperature of 0° C. for 5 hrs. If the oil has been properly treated in the winterizing process it will remain clear, brilliant, and limpid at the conclusion of the test.

IX—SOAP STOCK AND ACIDULATED SOAP STOCK

1. PRESERVATION OF SAMPLES—To prevent fermentation and subsequent chemical decomposition in samples of soap stock and acidulated soap stock which are not intended for immediate analysis, 0.1 per cent of oil of cassia must be added and thoroughly mixed with such samples when drawn.

2. TOTAL FATTY ACID—(Not applicable to copra and palm kernel soap stock or acidulated soap stock of same, for which see 3.)

From a weighing bottle weigh out 8 or 10 g. of a well-mixed sample of cottonseed foots, or 4 to 5 g. of acidulated soap stock, and transfer the same to a 400 cc. beaker. Saponify with an excess of alcoholic sodium or potassium hydroxide and after saponification is complete, heat in a steam bath, with stirring, until all the alcohol is driven out. Add 200 to 250 cc. of distilled water and heat until the soap is completely dissolved. Acidify with dilute hydrochloric acid (1 : 1) using only a small excess, cover with a watch glass and continue heating until the fatty acid layer is clear. Cool the fatty acid layer until solid, filter off the liquor and wash thoroughly with cold water. Allow the washed fatty acids to dry, most conveniently overnight. Now dissolve the fatty acids in warm petroleum ether, which has a boiling point below 65° C., and make a total volume of approximately 125 cc. with the solvent. Filter through a dry filter paper into a tared Soxhlet flask. Wash the filter with warm petroleum ether. Finally, evaporate off the petroleum ether, heat in an oven at 100° C. to constant weight, and report as percentage of total fatty acids.

3. METHOD FOR THE DETERMINATION OF THE TOTAL FATTY ACIDS AND UNSAPONIFIABLE MATTER OF COCONUT OILS AND PALM KERNEL OILS—From a weighing bottle weigh out a sample which will furnish approximately 5 g. of fatty acids. Saponify in a 250 cc. beaker, using 50 cc. of 95 per cent alcohol and 2 to 3 g. of stick potassium hydroxide, or an equivalent of a stock solution of potassium or sodium hydroxide. Heat on a steam bath, with occasional stirring, until saponification is complete; then evaporate off the alcohol. This evaporation is facilitated by a current of filtered air. When the alcohol is evaporated, add 100 cc. of water and heat until the soap is dissolved. Wash the contents of the beaker into an extraction cylinder with hot water, taking care to use no more than 130 cc. The glass cylinder must be glass stoppered, graduated at 40 cc., 80 cc., and 130 cc., have a diameter of approximately 1.375 in. and a height of about 12 in. Acidify with dilute hydrochloric acid (1 : 1), being careful to avoid too large an excess. Mix by gently rotating the cylinder and when it has cooled to about 50° C. add 50 cc. of petroleum ether. It is not necessary for the fatty acids to have cleared thoroughly. Stopper the cylinder and shake; then allow it to stand until the petroleum ether layer has separated. Syphon off the petroleum ether through a 9 cm. filter paper into a 600 cc. beaker. Make at least four more extractions, using from 25 to 30 cc. of petroleum ether each time. Allow the filter to drain well; then wash with a spray of petroleum ether from a wash bottle until all the fatty acids are extracted. Add 50 cc. of 95 per cent ethyl alcohol, redistilled from caustic, to which a few drops of phenolphthalein have been added. Titrate with *N* sodium hydroxide, evaporate off the petroleum ether on a steam bath, then concentrate until the volume is reduced to about 25 to 30 cc., and transfer with hot 95 per cent alcohol redistilled from caustic to a 250 cc. beaker, tared, including a stirring rod. Finally, evaporate and dry in an oven at 105° to 110° C. to constant weight. In order to calculate the soda soap to fatty acids, a correction must first be made for the neutral salts in the caustic solution. To do this, neutralize 20 cc. of normal caustic soda with 0.5 *N* hydrochloric acid, using a small amount of phenolphthalein as indicator. Evaporate to dryness. Heat to constant weight at 105° to 110° C. and from the weight of the residue found subtract the weight of salt calculated. The difference divided by 200 gives the correction per cubic centimeter for neutral salts. From the weight of the soda soap subtract the product of the titration of the fatty acids, multiply by the factor (0.022 plus correction for neutral salts), divide the result by the weight of sample used, and multiply by 100, which gives the result to be reported as percentages of total fatty acids and unsaponifiable matter.

X—TITER

The method to be employed is that for fat given in THIS JOURNAL, 11 (1919), 1163, under "Standard Methods for the Sampling and Analysis of Commercial Fats and Oils."

XI—ALL OTHER TESTS

In the case of tests not covered by these standard methods, the methods of the AMERICAN CHEMICAL SOCIETY are to apply, and in cases where such methods have not been provided by the SOCIETY, those of the Association of Official Agricultural Chemists[1] shall be considered satisfactory methods.

APPENDIX—OIL GRADES[2]

CRUDE OIL

CHOICE CRUDE cottonseed oil must be made from sound decorticated seed; must be sweet in flavor and odor, free from water and settlings, and shall produce, when properly refined, choice summer yellow oil at a loss in weight not exceeding six per cent.

PRIME CRUDE cottonseed oil must be made from sound decorticated seed; must be sweet in flavor and odor, free from water and settlings and must produce prime summer yellow oil with the use of caustic soda by the official methods adopted by the Chemists Committee, with a loss in weight not exceeding 9 per cent; provided, that any oil that refines with a greater loss than 9 per cent, but still makes prime summer yellow oil, shall not be rejected, but shall be reduced in price by a corresponding percentage of the contract price of the oil.

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[1] Published by the Association of Official Agricultural Chemists, Washington, D. C.

[2] Adopted by the Interstate Cottonseed Crushers' Association.

OFF-CRUDE cottonseed oil, if neither choice nor prime, shall be called "Off Oil."

REFINED OIL

CHOICE SUMMER YELLOW cottonseed oil must be sweet in flavor and odor, prime in color, clear and brilliant in appearance and free from moisture.

PRIME SUMMER YELLOW cottonseed oil must be clear, sweet in flavor and odor, free from water and settlings, and of no deeper color than 35 yellow and 7.6 red on Lovibond's equivalent color scale.

PRIME WINTER YELLOW cottonseed oil must be brilliant, free from water and settlings, sweet in flavor and odor, and of prime summer yellow color as described above. and must stand limpid at a temperature of 32° F. for 5 hrs.

GOOD OFF SUMMER YELLOW cottonseed oil may be off in flavor and odor, must be prime in color and free from water and settlings, and shall not contain more than 0.25 per cent of free fatty acid.

OFF SUMMER YELLOW cottonseed oil shall be free from water and settlings, off in flavor or odor, but of no deeper color than 35 yellow and 12 red on Lovibond's color scale and shall not contain more than 0.5 per cent of free fatty acid.

REDDISH OFF SUMMER cottonseed oil, designated as such, may be of inferior flavor and odor and of no deeper color than 35 yellow and 20 red on Lovibond's equivalent color scale, shall be free from water and settlings and shall not contain more than 0.75 per cent free from fatty acid.

BLEACHABLE PRIME SUMMER YELLOW cottonseed oil must be clear, sweet in flavor and odor, free from water and settlings, and when bleached shall be of no deeper color than 20 yellow and 2.5 red on Lovibond's equivalent color scale.

PRIME SUMMER WHITE cottonseed oil must be clear, free from water and settlings, sweet in flavor and odor, and the color of the oil shall not be darker than the combined standard glasses, 20 yellow and 2.5 red, Lovibond's color scale.

PRIME WINTER WHITE cottonseed oil must be brilliant, sweet in flavor and odor, free from water and settlings, and the color of the oil shall not be darker than the combined standard glasses, 20 yellow and 2.5 red of Lovibond's color scale, and must stand the cold test as prescribed.

ANNUAL MEETING OF THE DIVISION OF CHEMISTRY AND CHEMICAL TECHNOLOGY, NATIONAL RESEARCH COUNCIL

The annual meeting of the Division of Chemistry and Chemical Technology, National Research Council, was held in Washington, D. C., May 7, 1920. There were present Messrs. Alsberg, Bancroft, Bleininger, Derick, Fink, Francis, Johnston, Lamb, Moore, Noyes, Stieglitz, Washburn; and by invitation Messrs. Angell, Christian, Cottrell, Kellogg, Mendenhall, Munroe, and Yerkes.

The following officers were elected for the ensuing year: Vice Chairman, Julius Stieglitz; Members-at-Large, A. A. Noyes, E. W. Washburn. The members of the Executive Committee will be the chairman and vice chairman, C. L. Alsberg, A. B. Lamb, John Johnston, and W. D. Bancroft, *ex officio*, retiring chairman. The AMERICAN CHEMICAL SOCIETY nominated C. L. Alsberg, W. D. Bancroft, and C. G. Derick as members of the division, and the American Institute of Chemical Engineers nominated H. K. Moore.

In connection with the meeting of the International Chemical Union to be held in Rome in June, Dr. Charles L. Parsons was appointed delegate. The admission to the Union of Poland and Czecho-Slovakia was favored, the division expressing the unanimous opinion that any neutral nation, eligible from the point of view of its scientific activities, that might apply for admission should be admitted.

In presenting the report of the Committee on Synthetic Drugs, Julius Stieglitz, chairman, pointed out the valuable work done by this committee in furnishing information and advice to manufacturers. The committee on request had acted in advisory capacity to the Chemical Foundation, which controls most of the important formerly foreign-owned patents. The committee was convinced that real service could be rendered, particularly to the organic chemical industries, through the existence of such a committee of unbiased men of scientific training and of experience in public affairs without any trade interests. The committee was continued for another year.

The report of the Committee on Explosives Investigations was presented by the chairman, Professor Charles E. Munroe. The following excerpts from the report indicate the various lines of activity of the committee:

> The committee has been engaged in arranging for, coöperating with or supervising investigations on the corrosion of rifle barrels; the development of Neumann Bands in metals subjected to exposure to the detonation of explosives of known rates or to blows from impact machines with a view to ascertaining if these bands may be used as a means of determining whether a fracture in metal is due to mechanical stress or strain or to the effects of an explosive; the utilization of surplus military explosives (1) by developing their adaptabilities for employment as explosives in industries; (2) by determining their availability for use as or conversion into fertilizers; products of combustion and detonation of TNT; heats of combustion and detonation of TNT isomers; development of insensitiveness in TNT during storage; nitration of corn-cob cellulose; the fudging of ammonium nitrate and the effect of this material on the rate of detonation of gelatin dynamite; coefficient of expansion of nitroglycerin; determination of nitro-sucrose in the presence of nitroglycerin; production of flashless powder; coloring matter for special shell; water storage of explosives; premature explosion of nitroglycerin in oil well shooting; development of modified TNT; catalytic nitrations.
>
> The committee has served as an intermediary in effecting coöperative agreements for investigations and developments between the Bureau of Mines and the College of Agriculture of the University of Wisconsin; the Ordnance Department, U. S. A., and several of our universities; the Bureau of Mines and E. I. du Pont de Nemours & Co. It has served as a channel of communication and for transmission of documents and publications between our people and specialists in England, France, Italy, Canada, Australia, and India; also as a general bureau of information, it having been called upon for service by a large number of the divisions of the State, Treasury, War, Navy, Interior and Agricultural Departments, as well as by officials in the industries and by students preparing theses. The information card catalog has been continued and now contains about 4,000 cards.
>
> Following the expressed desire of the Council, Munroe's "Index to the Literature of Explosives" is now being brought up to 1907, at which date the publication of *Chemical Abstracts* was begun, and the completed manuscript has now been placed in the vault of the Council for the following journals: *Philosophical Transactions Royal Society*, 1665–1906; *American Journal of Science*, 1819–1906; *Proceedings U. S. Naval Institute*, 1878–1906; *Journal Society of Chemical Industry*, 1882–1906.

As a result of this coöperation, various articles have appeared in scientific publications.

The Committee on the Thermal Properties of Explosive Materials was not continued, the work being transferred to the Committee on Explosives Investigations. This latter committee was requested to associate with itself W. P. White and others interested in the study of the thermal properties of explosives.

In the absence of H. N. Holmes, chairman of the Committee on Colloids, the report of the committee was presented by W. D. Bancroft. This report gave an account of the courses of lectures given at universities, industrial plants, government bureaus, and local sections of the AMERICAN CHEMICAL SOCIETY by W. D. Bancroft, H. N. Holmes, W. A. Patrick, I. N. Kugelmass, and Martin Fisher. The need of suitable texts and laboratory manuals for the teaching of colloid chemistry was emphasized and the announcement made that W. D. Bancroft now has in preparation a textbook soon to be published, while a laboratory manual is being prepared by H. N. Holmes. A detailed classified bibliography on colloid literature is being compiled which it is hoped to publish later. A small manual for the use of the ultramicroscope is being prepared by Jerome Alexander.

Following remarks by John M. Francis, the Committee on Pharmaceutical Research was authorized and requested to formulate a program of research. The report of the Committee on Ceramic Research was read and the committee continued for another year.

Owing to delays in getting organized, the Committee on Sewage Disposal, of which Edward Bartow is chairman, had no report, but as definite plans for future activity of the committee were being formulated, the committee was continued for another year.

Upon the suggestion of C. G. Derick, a Committee on Methods of Organic Analysis was appointed.

The need for coöperation between the various laboratories and individuals working on contact catalysis was pointed out by Chairman Bancroft, and as a result a Committee on Contact Catalysis was appointed, with W. D. Bancroft as chairman.

The report of the Board of Trustees for the Publication of Critical Tables of Physical and Chemical Constants was presented by H. K. Moore. The Council approved the suggestion that a special agent be employed to devote his entire time to the solicitation of funds for this publication. Thereupon H. E. Howe was appointed a fourth member of the Board of Trustees; W. D. Bancroft and C. E. Mendenhall were authorized to pay for the drawing up of a preliminary plan for the scientific organization of the Tables, as a concrete basis for obtaining subscriptions. C. G. Derick called attention to the need of constants in the dye industry to determine the purity of materials.

Dr. Cottrell was appointed to draw up a resolution in support of the Patent bill, with instructions to forward the resolution to the Patent Office Committee of the National Research Council for such action as it saw fit to take.

PRESENTATION OF HONORARY MEMBERSHIP CERTIFICATE TO M. ERNEST SOLVAY

On May 27, 1920, in the city of Brussels, the United States Ambassador, Hon. Brand Whitlock, in company with Dr. Charles L. Parsons, Secretary of the American Chemical Society, presented to M. Ernest Solvay, on behalf of the Society, an engrossed certificate of honorary membership, carrying the Society's seal and colors. M. Solvay, though 83 years of age, is in vigorous health, as is evidenced by the fact that he walks five miles each day from his country place, reaching his office at 8 A. M. M. Solvay was deeply appreciative of the honor of honorary membership and the method of its presentation.

U. S. PHARMACOPOEIAL CONVENTION, CENTENNIAL MEETING

The eleventh decennial United States Pharmacopoeial Convention met at the New Willard Hotel, Washington, D. C., on May 11 to 13, 1920, celebrating the centennial of our national pharmacopoeia and arranging for the new revision of that standard of drugs and medicines.

An outstanding feature of the convention was the presidential address of Harvey W. Wiley, in which he described the first convention (that of 1820) and cited the sacrifices made by the pharmacopoeia makers of the intervening century; and outlined the ideals that should govern the coming revision.

Other important business transacted was the election of officers, trustees, and members of the Revision Committee of fifty, and the adoption of general principles upon which the forthcoming revision will be based.

The newly elected president of the convention is Dr. Reid Hunt, of Harvard Medical School, while Dr. James H. Beal, of Urbana, Illinois, was re-elected chairman of the trustees.

The committee of fifty elected to carry on the revision consists of seventeen members chosen by the medical delegates and thirty-three chosen by the pharmaceutical delegates. The following members of the American Chemical Society were among those chosen by the pharmaceutical delegates:

C. L. Alsberg
H. V. Arny
G. M Beringer
T. J. Bradley
C. E. Caspari
A. H. Clark
E. F. Cook
A. R. L. Dohme
A. G. DuMez
F. R. Eldred
J. M. Francis
L. B. Havenhill
C. B. Jordan
C. W. Johnson
Henry Kraemer
C. H. LaWall
B. L. Murray
E. L. Newcomb
F. W. Nitardy
W. O. Richtman
G D. Rosengarten
W. L. Scoville

Two of the three delegates to the convention from the American Chemical Society were selected as members of the Revision Committee, while the chairman of the five sub-committees most concerned in the chemicals of the pharmacopoeia are likewise members of the Society. These are H. V. Arny (inorganic chemicals), G. D. Rosengarten (organic chemicals), C. H. LaWall (reagents and test solutions), W. O. Richtman (volatile oils), and C. E. Caspari (drug assays). E. Fullerton Cook, of Philadelphia, was elected chairman of the Revision Committee.

The convention adjourned on May 13 to meet next in May 1930.

MANUFACTURING CHEMISTS' ASSOCIATION

At the annual meeting of the Manufacturing Chemists' Association of the United States, held June 9, 1920, the following officers were elected: President, Dr. Charles L. Reese, of E. I. du Pont de Nemours & Co.; vice presidents, H. H. S. Handy, of the Semet-Solvay Company, and C. Wilbur Miller, of the Davison Chemical Company; treasurer, Lindsley Loring, vice president of the Merrimac Chemical Company; secretary, Arthur H. Weed, 84 State St., Boston; executive committee, Henry Howard, of the Grasselli Chemical Company, Lancaster Morgan, of the General Chemical Company, H. H. Dow, of the Dow Chemical Company, Adolph Rosengarten, of the Powers-Weightman-Rosengarten Company, Mr. Miller, and D. W. Jayne, of The Barrett Company. The chief business concerned the annual report of the executive committee, which emphasized the success of the committee in coöperating with the Chemical Foundation, and gave particular attention to the progress of dye legislation. In spite of the discouraging delays, the Association is confident of the ultimate adoption by Congress of adequate protective legislation. The work of the National Industrial Conference Board, particularly in the campaign for the revision of the tax laws, was commended.

CALENDAR OF MEETINGS

Insecticide and Disinfectant Manufacturers' Association—Midsummer Meeting, Boston, Mass., July 15 and 16, 1920.

Forest Products Laboratory Decennial Celebration—Madison, Wis., July 22 and 23, 1920.

American Chemical Society—Sixtieth (Annual) Meeting, Chicago, Ill., September 7 to 10, 1920.

Sixth National Exposition of Chemical Industries—Grand Central Palace, New York, N. Y., September 20 to 25, 1920.

NOTES AND CORRESPONDENCE

UNSAPONIFIABLE MATTERS

Editor of the Journal of Industrial and Engineering Chemistry:

In This Journal, 11 (1919), 1161, is given the final report of the Committee on Analysis of Commercial Fats and Oils of the Division of Industrial and Engineering Chemistry of the American Chemical Society, as adopted April 14, 1919, by unanimous vote.

Anyone who has served on such a committee knows the great amount of work required of its members and the difficulty of harmonizing varying ideas, with the result that the final conclusions are apt, to some extent, to be compromises. Owing to the difficulties of getting members together and actually illustrating certain points by tests, all points cannot be satisfactorily worked out, without unduly prolonging the time required to make a report.

We wish here to call particular attention to the method adopted for the determination of unsaponifiable matters. Although this method is better than any other published commercial method with which we are acquainted, in that it is easy to carry out and gives fairly concordant results, it contains a source of error which may not be constant, and which is very easily eliminated with practically no additional work. We refer to the presence of free fatty acids in the final residue recorded as "unsaponifiable matter." By the method of extraction and washing employed this final residue always contains more or less free fatty acids, yet the committee made no mention of the fact nor suggested any method of correction. Although this point was called to the attention of the committee and illustrated by examples, they did not see fit to add to their method the operation which would eliminate the error in question.

During the petroleum ether extractions the amount of alcohol in the solution are not over 30 per cent by volume. Fifty per cent of alcohol are required to prevent hydrolysis of most soap solutions. Therefore, unless there is a sufficient excess of alkali at this point, the soap is bound to undergo hydrolysis to some extent, with the result that the petroleum ether extracts will contain some free fatty acids. They will also, probably, contain some soaps. The combined extracts are washed with 10 per cent alcohol washes, with the result that any soaps present in the petroleum ether extracts may undergo some hydrolysis. The final residue is, therefore, bound to contain free fatty acids, and not necessarily in constant proportional amounts. Actual tests show this to be the case.

Twitchell's method,[1] which is much the same as the committee method but employs ethyl ether for extraction, takes into account the free fatty acids left with the final residue and deducts their amount, calculated as oleic acid. The objection to this method is that these free fatty acids are not oleic acid, and in many cases a serious error is introduced by so considering them.

On trying the committee method we have always found the final residue to contain titratable amounts of free fatty acids, and it is obvious that any free fatty acids in this residue should be deducted from unsaponifiable matter. It might be claimed that the amount of free fatty acids would be practically constant and that they would make little difference in a commercial method. But the amount of free fatty acids left is not constant and the residue may contain more free fatty acids than it does true unsaponifiable matter.

Using the committee method as a basis, we modified the method of washing the petroleum ether extracts, by introducing a wash with dilute caustic solution, whereby free fatty acids are removed from the petroleum ether and hydrolysis of any soap prevented, at least to a great extent. Our residues contain either no titratable amounts of free fatty acids, or such small amounts that considering them as oleic acid will introduce no appreciable error.

Our method is as follows: Five g. of the fat or oil are saponified according to the committee method, which is followed in all details up to obtaining the petroleum ether extracts. The extracts are washed with 25 cc. portions of 10 per cent (10 cc. diluted to 100 cc.) alcohol as directed, then with 0.5 *N* sodium or potassium hydroxide solution, followed by 10 per cent alcohol again, and then with water until all alkali has been washed out. Determinations by the committee method and our modification are given below:

UNSAPONIFIABLE MATTER IN SOY-BEAN OIL BY COMMITTEE METHOD

Five petroleum ether extractions were made and the extracts combined before washing. After three washes with 10 per cent alcohol (25 cc. each time), the extracts were transferred to a weighed flask, the ether evaporated off, and the residue dried in an air oven at 105° C. for about half an hour, cooled, and weighed.

	Gram	Per cent
Residue recovered	0.0422	0.844
Free fatty acid titrated with 0.1 *N* NaOH (0.29 cc.), combining weight of 279 (found for pure soy-bean oil fatty acids)	0.0081	0.162
Net unsaponifiable matter		0.682

In a second test the method was modified to include a wash with dilute hydrochloric acid, as in Twitchell's method.

	Gram	Per cent
Residue recovered	0.0532	1.064
Free fatty acid titrated as before (0.72 cc.)	0.0201	0.402
Net unsaponifiable matter		0.662

MODIFICATION OF THE COMMITTEE METHOD

Five grams of oil were saponified as directed by the committee, and their method followed until after the first set of alcohol washes. The extract was then washed with 25 cc. of 0.5 *N* sodium hydroxide solution, followed by alcohol washes and water until alkali was all washed out.

	Gram	Per cent
Residue recovered (No 0.1 *N* NaOH required for free fatty acids)	0.0337	0.6740

A second test followed, modified to include a wash with dilute hydrochloric acid after the first set of alcohol washes, followed by our regular method, including an alkaline wash.

	Gram	Per cent
Residue obtained (No 0.1 *N* NaOH required for any free fatty acids left in residue)	0.0325	0.6500

These illustrations are sufficient to show that free fatty acids are left in the residue obtained by the committee method, while by our modification no titratable amount of free fatty acids is left in most cases, but sometimes there are very small amounts. When we heat the residues with neutral alcohol, add phenolphthalein and one drop, or a fraction of a drop, of 0.1 *N* sodium hydroxide and obtain a strong permanent red coloration, we consider that there is no titratable amount of free fatty acids present.

The above matter illustrates our point, but it may be of interest to compare the above methods with a similar method, using ethyl ether instead of petroleum ether for extractions.

It is to be noted that ether always gives higher results than petroleum ether. This is to be expected, as petroleum ether is a poorer solvent than ether for oxidized and hydroxy fatty matters. Ether probably gives more accurate results, but for a commercial method petroleum ether appears more satisfactory.

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[1] This Journal, 7 (1915), 217.

TEST I—Five grams were saponified as usual, transferred to an extraction cylinder, made up to 40 cc. with alcohol, treated with 120 cc. of water and 50 cc. of purified (water- and alcohol-free) ether, shaken, and separated. After five extractions the ether extracts were joined and washed with dilute hydrochloric acid as in Twitchell's method, then with N KOH, and then with water until free from alkali.

	Gram	Per cent
Residue obtained..................	0.0445	0.8900
Free fatty acid titrated with 0.1 N NaOH........................	0.0056	0.1116
Net unsaponifiable matter.......		0.7784

Test II—This was a duplicate of Test I.

	Gram	Per cent
Residue obtained..................	0.0450	0.90
Free fatty acids....................	0.0056	0.11
Net unsaponifiable matter........		0.79

TEST III—This was the same as Tests I and II, except that 75 cc. of ether were used the first time and three additional 50 cc. extractions were made.

	Gram	Per cent
Residue obtained..................	0.0498	0.9960
Free fatty acid.....................	0.0073	0.1460
Net unsaponifiable matter........		0.850

TEST IV—This was the same as Test III, except that a wash with hydrochloric acid was included.

	Per cent
Corrected unsaponifiable matter....................	0.8361

DRY EXTRACTION METHOD

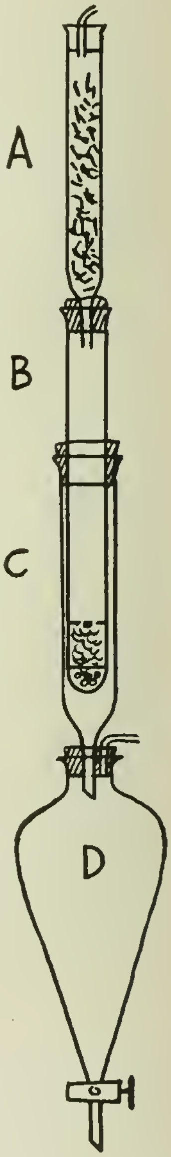
Comparison with a dry extraction method may be of interest, particularly in connection with another extraction of soy-bean oil of which we will speak later. Our method of making a dry extraction uses a special arrangement of apparatus and ethyl ether purified from water and alcohol. This is obtained by adding a good excess of dry granular calcium chloride, shaking well at intervals, and allowing to stand overnight. Filter off the ether (protecting from circulation of air) and to each liter of ether add 50 g. of dry rosin and distil off the ether. The apparatus is illustrated.

GENERAL METHOD OF OPERATION—The fat or oil is saponified by boiling with excess of alcoholic alkali, the alcohol evaporated off, and drying finished in a vacuum oven at as high a heat as the material will stand. When perfectly dry and free from alcohol (usually within a short time) the material is mixed with at least twice its weight of dry soda ash and finely ground in a glass mortar and placed in the extraction tube. About 75 cc. of ether, purified from water and alcohol, are run in on top of the material to be extracted and allowed to percolate through it. The percolate will generally be so strong in unsaponifiable matter by the time it reaches the end of this tube that it is ready to crystallize. After one or two percolations the material is removed from the tube, dried for a short time, and repulverized to expose new surfaces. This is the only drawback to the dry extraction method, but is not as much trouble as it would appear. There is generally no trouble with the percolation, if the ether is properly purified, but suction may be used, if necessary.

APPLICATION TO SOY-BEAN OIL—Five grams of the oil were saponified as usual, the alcohol driven off, and the resulting mass dried and mixed with 20 g. of anhydrous sodium carbonate, ground finely in a mortar and put in the tube. One hundred and fifty cc. of purified ether were used for the first extraction. Percolation was steady and became faster as extraction proceeded. Each ether extract was washed first with neutral water to see if there was any indication of alkali in solution, as shown by phenolphthalein. A little was shown each time, but with other stocks these extracts are often free from any soap or other alkali. The water wash was then followed by a wash with 0.5 N NaOH solution to remove any soaps and prevent hydrolysis as much as possible. Finally all sodium hydroxide was washed out with pure water and the matter remaining in solution recovered.

	Gram	Per cent
First extract with 150 cc. dry ether.....	0.0541	1.082
Free fatty acids, 0.03 cc. 0.1 N NaOH.	0.0008	0.016
Net unsaponifiable.................	0.0533	1.066
Reground mixture and extracted again:		
Second extract with 150 cc. dry ether...	0.0035	0.070
No free fatty acid indicated.		
Reground again:		
Third extract with 150 cc. dry ether....	0.0018	
Free fatty acid, 0.05 cc., 0.1 N NaOH..	0.0014	
Net unsaponifiable.................	0.0004	0.008
Reground again:		
Fourth extract with 150 cc. dry ether...	0.0004	0.008
Free fatty acid too small to titrate		
Total unsaponifiable matter.........		1.150

To all appearances the unsaponifiable matter obtained by the dry method was the same as that obtained by the wet method referred to below. It is noticeable how much higher the unsaponifiable matter is than is shown by either the committee method or by our modification.



A—Large tube filled with granular calcium chloride, to keep moisture of air from entering apparatus

B—Extraction tube with several small holes through bottom. Into this tube is put the powder to be extracted. There is a plug of cotton wool in the bottom and a perforated lead plate just above it to hold it in place and make a seat for the substance to be extracted. It also facilitates removal of the substance for regrinding

C—Adapter to allow extraction tube to be connected with 500 cc. (or other size) separatory funnel

D—Squibb's form of separatory funnel. Proportions are about as shown, diameters of tubes varying from an inch to an inch and a half

WET EXTRACTION METHOD

WET EXTRACTION OF UNSAPONIFIABLE MATTER FROM SOY-BEAN OIL—Soy-bean oil was filtered through paper and 50 g. of the filtered oil used. Without going into details, the general method was to saponify with excess of alcoholic potash solution, and dilute with water so that the resulting solution would contain about one-fourth of its volume of alcohol. After making about three ether extractions at this dilution, more water was added to reduce the alcohol content to about one-sixth of the total volume, and further extractions with ethyl ether were made. The various residues obtained were reboiled with excess of alcoholic potash and the unsaponifiable matter reëxtracted. Unfortunately the first and main residue was not tested for free fatty acids, and so probably appears higher than it should, and the spread, after resaponification and extraction, is greater than it would be had the fatty acids been deducted.

SUMMARY OF OPERATIONS

The residue (uncorrected for free fatty acids) amounted to 1.16 per cent unsaponifiable matter, which checks with that found by the dry method, which, however, was corrected for any free fatty acids. This residue was resaponified with the following results:

	Per cent from 1/4 alcohol	Per cent from 1/6 alcohol	Per cent Total
	1.1500	0.0100	1.1600
Recovered upon first resaponification.........	0.8420	0.0036	0.8456
Recovered upon second resaponification.......	0.7840	....	0.7840
Recovered upon third resaponification......	9.7183	0.0240	0.7423
Recovered upon fourth resaponification.......	0.6770	trace	0.6770

It is evident that we have continually lost weight and it would seem that this loss cannot be satisfactorily explained by failure to extract each time the full amount of unsaponifiable matter left, but rather points to the action of alcoholic alkali on the residues, either in decomposing some of the true unsaponifiable matter or in completing the saponification of some very difficultly saponifiable matter, which would then be present in all ordinary residues and reckoned as unsaponifiable matter. The resaponifications and reëxtractions were stopped at the above point because the amount of free fatty acids to be corrected for had apparently reached a constant figure in the last two cases. Whether this was the true end we doubt. The point happens to give the same final result as the determination by the committee method, but this may be considered only a coincidence.

THE CUDAHY PACKING COMPANY
OMAHA, NEBRASKA
December 15, 1919

WILSON H. LOW

....

Editor of the Journal of Industrial and Engineering Chemistry:

Mr. Low's remarks in the early part of his paper, entitled "Unsaponifiable Matters," on the difficulties which confront committees working on analytical methods are interesting but do not apply to the committee of which I am chairman. This committee made a practice of meeting regularly once a month during its period of greatest activity, and thereafter meetings were held whenever a sufficient number of results from coöperative work had accumulated to warrant calling a meeting. Conferences in various laboratories were held from time to time for the purpose of coöperating on one or another moot point in the various methods, several members of the committee meeting in this way first in one laboratory and then in another until the point was settled and unanimity reached. Such coöperative work was done on the unsaponifiable method.

It is difficult for any committee to adopt a method of analysis satisfactory to all workers and this is perhaps particularly true of the unsaponifiable determination. In my opinion, however, the method finally adopted by the committee in point of accuracy, convenience, simplicity, speed, and reliability in various hands comes as near perfection as we can hope for in the present state of our knowledge.

The point which Mr. Low discusses was brought to the committee's attention by him. After careful consideration the committee decided that it was not necessary to add the manipulation advocated by Mr. Low. Mr. Low states that "By the method of extraction and washing employed this final residue always contains more or less free fatty acids, yet the committee made no mention of the fact nor suggested any method of correction." The answer to this statement is that the amount retained is very small; so small, in fact, as to make no appreciable difference in the results, particularly for commercial purposes. In the majority of samples of oils, fats and greases the amount of free fatty acids at this point usually varies from 0.02 to 0.07 per cent, rarely it amounts to as much as 0.1 per cent, and the high figures are generally found in the case of an oil whose general peculiarities are well known—soy-bean oil. Considered as an absolute error on the positive side, this amount is not great and not worth taking into consideration in the commercial analysis of oils and fats. On the other hand, from the point of view that it may be a counter-balancing error working against incomplete extraction, it is of still less moment. Good manipulation reduces the amount, poor manipulation increases it. Judging by his own figures in comparison with the results by members of the Fat Analysis Committee, Mr. Low's manipulation is open to criticism.

Mr. H. J. Morrison, of the Procter and Gamble Company, writes as follows in regards to Mr. Low's argument:

> I have read over carefully Mr. Low's paper in which he criticizes the method for determining the unsaponifiable matter in the Standard Methods for the Analysis of Commercial Fats and Oils.
>
> Mr. Low's paper is worded unfortunately in that one gets the impression that the committee did not accept criticisms and did nothing to investigate them. This, of course, is quite wide of the mark.
>
> On that particular point raised by Mr. Low I believe we did more work than on any other point raised by outside criticism. The committee was quite alive to the danger of high results due to hydrolysis. One point which we discussed was the amount of caustic alkali to be used for the saponification, and the amount was fixed at a very large excess over the theoretical for the purpose of rapid and complete saponification, on the one hand, and to have an excess present to prevent hydrolysis when diluted for extraction, on the other hand. Mr. Low mentions an excess as a preventive of hydrolysis but either has not calculated the amount of excess the method calls for or must consider a very excessive amount necessary to prevent hydrolysis.
>
> Doubtless Mr. Low has many more than the one analysis by the committee method on which he bases his contention that a serious error is introduced by this hydrolysis. From the experience of this laboratory I cannot help but feel that the source of Mr. Low's error is due to faulty technique In order to protect our results from carelessness we have practiced having the unsaponifiable titrated and in 445 such titrations on the great variety of fats, oils and greases which pass through our laboratory the average titration was 0.076 cc. 0.1 *N* NaOH, equal on 5 g. of fat to 0.04 per cent. This is quite within the limit of error of this particular operation, and I may point out that these 445 results are of course the daily routine analyses, by routine men such as are employed in such laboratories.
>
> Mr. Low seems to explain the error and its necessary correction in the ethyl ether extraction method by the hydrolysis theory. This is not at all the case as I think we demonstrated. It is due to actual solution of soap, owing to the solubility of both water and alcohol in the ethyl ether phase. Mr. Low's error when using the committee method, as stated above, is due, I believe, to technique, possibly by not allowing sufficient time for a thorough separation or by drawing off the petroleum ether extract too close.
>
> I am not going to enter a discussion here concerning the other methods Mr. Low speaks of, as I think it patent to anyone conversant with fats and their analysis wherein they cannot give correct results. Our committee, I believe, cannot be accused of not trying out any suggestions and I feel are willing now at any time to try out anything which promises an improvement, but I feel that this should be done by direct appeal to the committee and not by the method of rushing into print, unless the author has irrefutable proof.

The amount of free fatty acids left in the final residue is usually neutralized by one drop of 0.1 *N* alkali. The one drop of 0.1 *N* alkali may or may not be an excess but frequently does amount to an excess. This point is indicated in Mr. Morrison's letter and is considered more at length in a letter received from Mr. Rudnick, of Armour and Company's laboratory, which follows:

> The assumptions made in the first paragraph of the paper by Wilson H. Low on unsaponifiable matters are not warranted by the facts. The methods adopted by the Fat and Oil Committee were not based merely on ideas, but on the outcome of actual tests, so that the final conclusions are not compromises of varying ideas. Indeed the outcome of the coöperative work done by the committee more than once upset long-held views

and while these views were sometimes abandoned with reluctance, in the end the votes of the members were always based on the facts developed.

This committee had no particular difficulty in point of attendance of its members. Occasionally differences in results became apparently irreconcilable by the usual coöperative procedure and in such cases special subcommittees were appointed to carry out the required tests jointly in the several laboratories in order to develop under personal observation the facts necessary to cover the disputed points.

None of the members of the committee reported any unusual difficulties in determining the unsaponifiable matter in soy-bean oil, to which the entire discussion in Low's paper is devoted, although it is well understood that some samples of soy-bean oil show an erratic behavior in other respects, notably in the determination of the titer.

It is difficult to see how any sound criticism of the committee method for determining unsaponifiable matter can be based on the data presented in Mr. Low's paper. The total amount of unsaponifiable matter obtained by him in accordance with the committee method and without applying his corrections for fatty acids, is well within the normal limits for natural unsaponifiable matter in soy-bean oil.

In order to determine, however, whether such corrections as described by him were true of other samples of soy-bean oil than the one on which he reports, a sample of crude oil was tested in this laboratory with the following results:

Weight of Sample	Unsaponifiable Matter Gram	Per cent
5.015 grams	0.050	1.00
5.012 grams	0.056	1.11
Mean		1.06

Fifty milligrams of unsaponifiable matter is a very small amount to titrate for free fatty acids and it was therefore not surprising that titration with 0.1 *N* alkali, observing the precautions directed in the committee method, should amount to 0.4 cc., equivalent to 0.22 per cent of free fatty acids, calculated as oleic, on the basis of the weight of the first sample.

On repeating the titration with 0.02 *N* alkali and carrying along a blank titration, matching as closely as possible the final color of the phenolphthalein, the net titration amounted to 0.72 cc. of 0.02 *N* alkali, equivalent to 0.08 per cent of free fatty acids, calculated as oleic, on the basis of the weight of the second sample.

It would seem, therefore, that if the corrections developed in Low's paper had been determined with a standard alkali of more appropriate concentration relative to the weight of material titrated, he might have obtained results on his sample of soy-bean oil of about the same order as those which the members of the committee obtained in their original coöperative work on which the method adopted was based.

There is nothing new in the work described in Low's paper on the Twitchell and the dry extraction methods. Both these methods were thoroughly tested by the committee and were rejected on the basis of the results obtained with them in coöperative work

Summing up, there seems to be no good ground for criticism of the committee method for determining unsaponifiable matter, either on the basis of the data presented in this paper or the method by which they were obtained.

Mr. Low speaks of Twitchell's method "which is much the same as the committee method." Anyone who is acquainted with the two methods must realize that the methods are distinctly and decidedly different in principle.

As to the dry extraction method mentioned by Mr. Low, this has been tried out in this laboratory off and on for the past fifteen years and has been found on the whole to be inaccurate and unreliable. The Committee on the Analysis of Commercial Fats and Oils also tried the method out and arrived at the conclusion that the method was wholly impossible and had no place among modern methods of analysis.

Since the adoption of the committee method, agreements on unsaponifiable determinations which were impossible before, have been reached between various laboratories and the method has proved a great advantage to the oil and fat trade.

The committee does not consider the additional alkali wash advocated by Mr. Low as either necessary or desirable if the committee method is followed and a moderate degree of skill acquired in manipulation.

Chemical Laboratory of
Swift & Company
Chicago, Illinois
March 31, 1920

W. D. Richardson,
Chairman, Committee on the Analysis of Commercial Fats and Oils

AWARDS FOR THESES ON FOODS AND BEVERAGES

In order to stimulate more general research along the lines of better preparation and packing of foods and beverages, and to increase our knowledge of changes induced by preparation or storage of food products, Dr. A. W. Bitting, Director of Research of the Glass Container Association of America, Chicago, Ill., has announced that awards will be made for theses on these subjects.

A thesis may cover any phase of the subject of foods or beverages—technological, bacteriological, or chemical. It may treat of any legitimate method of preparation, as sterilization by heat, pasteurization, salting, drying, smoking, pickling, sugaring, etc., the product to be packed in glass. The thesis may be bibliographical with abstracts, or may be a translation from work along the lines indicated. It must be submitted prior to June 10, 1921.

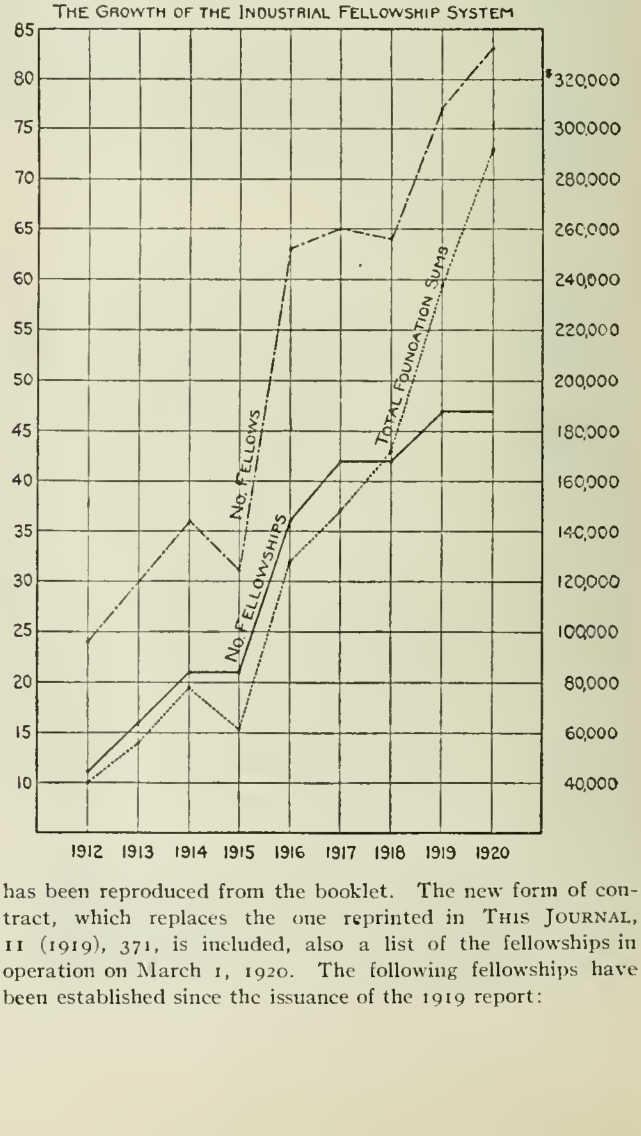
The awards will be as follows:

One	$150
One	125
One	100
Two	75
Two	50

Any student or graduate student working for a degree in any college or university is eligible to compete. The awards will be made by a competent committee and as soon after June 10, 1921, as practicable.

THE INDUSTRIAL FELLOWSHIPS OF THE MELLON INSTITUTE

Under the above title there has been issued recently by the Director of the Mellon Institute for Industrial Research, Dr. Raymond F. Bacon, an attractive pamphlet covering the progress of the industrial fellowship system during the past fiscal year. The growth of the Institute's system is described in detail and shown graphically in the accompanying figure, which has been reproduced from the booklet. The new form of contract, which replaces the one reprinted in This Journal, 11 (1919), 371, is included, also a list of the fellowships in operation on March 1, 1920. The following fellowships have been established since the issuance of the 1919 report:



No.	Names of Industrial Fellowships	Industrial Fellows, Names and Degrees	Foundation Sums and Dates of Expiration
192	Enameling	R. D. Cooke (M.S., University of Wisconsin)	$3,000 a year. April 1, 1920
193	Leather Belting	P. G. McVetty (M.E., Cornell University), Senior Fellow M. J. Pooley (B.S., Dakota Wesleyan University)	$5,650 a year. April 1, 1920
195	Protected Metals	J. H. Young (Ph.D., Ohio State University)	$4,500 a year. June 1, 1920
196	Collar	H. D. Clayton (B.A., Ohio State University)	$3,300 a year. May 1, 1920
197	Sulfur	H. S. Davis (Ph.D., Harvard University) Mary D. Davis, assistant (B.A., Dalhousie University) C. N. Wenrich, assistant (Ph.D., University of Pennsylvania)	$7,200 a year. June 1, 1920
198	Dental Products	C. C. Vogt (Ph.D., Ohio State University)	$2,400 a year. July 1, 1920. Bonus royalty on sales
199	Copper	C. L. Perkins (B.S., New Hampshire College) R. E. Sayre (M.S., University of Wisconsin)	$6,500 a year. July 1, 1920
200	Physiological Research	K. K. Jones (M.S., Kansas State Agricultural College)	$5,500 a year. August 1, 1920
201	Quartz	William Stericker (B.S., University of Wisconsin)	$2,100 a year. September 8, 1920
202	Oil	W. F. Faragher (Ph.D., University of Kansas), Senior Fellow W. A. Gruse (Ph D., University of Wisconsin) F. H. Garner (M S., Birmingham University)	$10,000 a year. September 1, 1920 Bonus, $10,000
203	Glass	R. R. Shively (Ph D., University of Pittsburgh)	$4,100 a year. September 1, 1920
204	Gas	J. B. Garner (Ph.D., University of Chicago), Senior Fellow R. W. Miller (Ph.D., University of Pittsburgh)	$7,500 a year. September 15, 1920
205	Yeast	F. M. Hildebrandt (Ph.D., Johns Hopkins University) G. S. Bratton (B.A., University of Tennessee) Madalyne S. Schairer, assistant (B.A., Vassar College) H. C. Hoover, assistant (B.A., Ursinus College)	$15,000 a year. November 1, 1920
206	Illuminating Glass	A. H. Stewart (B.A., Washington & Jefferson College)	$3,000 a year. October 1, 1921
207	Glycerol	Melvin DeGroote (B.Ch E., Ohio State University)	$4,000 a year. November 15, 1920
208	Fiber	J. D. Malcolmson (B.S., University of Kansas)	$4,500 a year. November 15, 1920
209	Household Utilities	F. F. Rupert (Ph.D., Massachusetts Institute of Technology) E. R. Edson (B.A., Clark College)	$6,000 a year. November 1, 1920
210	Zirconium	J. H. Becque (M.S., Rose Polytechnic Institute)	$4,000 a year. November 15, 1920
211	Fish Products	D. K. Tressler (Ph D., Cornell University)	$4,000 a year. April 1, 1921
212	Copper	G. A. Bragg (B.S., University of Kansas)	$6,000 a year November 1, 1920
213	Silicate	J. L. Crawford (B S., University of Illinois)	$3,000 a year. December 1, 1920
214	Fuel	J. G. Davidson (Ph.D., Columbia University)	$5,000 a year. January 1, 1921
215	Silverware	H. E. Peck (B.S., Clarkson Memorial College of Technology)	$3,000 a year. December 11, 1920
216	Magnesia	T. S. Taylor (Ph.D., Yale University) R. H. Heilman, assistant (University of Pittsburgh)	$10,000 a year. January 1, 1921
217	Insecticides	O. F. Hedenburg (Ph.D., University of Chicago)	$4,200 a year January 1, 1921
218	Organic Solvents	(Senior Fellow to be appointed) H. W. Greider (M.S., University of Kansas)	$7,500 a year. January 1, 1921
219	Coke	F. W. Sperr, Jr. (B.A., Ohio State University), Advisory Senior Fellow O. O. Malleis (M.S., University of Kansas) R. L. Brown (Ph.D., University of Chicago) (A third Fellow to be appointed)	$5,580 a year. January 1, 1921
220	Organic Synthesis	G. O. Curme, Jr. (Ph.D., University of Chicago), Senior Fellow C. J. Herrly (B.S., Pennsylvania State College) J. N. Compton (Ch E., Rose Polytechnic Institute) E. W. Reid (N.S., University of Pittsburgh) C. O. Young (Ph.D., University of Pittsburgh) F. W. Hightower (B.A., University of Texas)	$41,000 a year. January 1, 1921
221	By-products	Walther Riddle (Ph.D., University of Heidelberg) H. E. Gill, assistant (B.Chem., University of Pittsburgh)	$3,000 a year. January 1, 1921
222	Fertilizer	H. H. Meyers (B.S., University of Pennsylvania), Senior Fellow W. E. Vawter (B.S., University of Kansas)	$8,000 a year. January 5, 1921 Bonus, $5,000
223	Glue	R. H. Bogue (Ph D., University of Pittsburgh)	$4,000 a year. January 5, 1921
224	Metalware	W. G. Imhoff (B.A., University of Wisconsin)	$5,000 a year. February 16, 1921
225	Distillation	David Drogin (M.S., University of Pittsburgh) Isaac Drogin (Ph.D., University of Pittsburgh)	$5,000 a year. January 18, 1921
226	Fruit Beverages	H. A. Noyes (M.S., Massachusetts Agricultural College)	$4,000 a year. March 1, 1921
227	Plastics	(Fellows to be appointed)	$7,000 a year.
228	Soap	O. H. Schunk (B.S., University of Wisconsin)	$2,500 a year. March 1, 1921
229	Laundry	H. G. Elledge (M.S., University of Pittsburgh), Senior Fellow Alice L. Wakefield (B.S., Carnegie Institute of Technology)	$6,400 a year. February 15, 1921
230	Refractories	R. M. Howe (M.A., University of Pittsburgh), Senior Fellow S. M. Phelps (University of Toronto) Mark Sheppard (B.S., Alfred University) R. F. Ferguson (B.S., University of Pittsburgh)	$12,000 a year. March 1, 1921. Bonus, $2,000
231	Keratin	(Fellow to be appointed)	$4,000 a year. Bonus, $5,000
232	Alloy	(Fellow to be appointed)	$3,500 a year.

CONSERVATION OF STANDARD SAMPLES OF THE BUREAU OF STANDARDS

Although Congress has failed to continue the appropriation for the work during the coming fiscal year, the Bureau of Standards will continue to prepare and issue standard samples. The money received from the sales of standard samples has always reverted directly to the Treasury, and is not available to the Bureau for any purpose whatsoever, therefore the cost of procuring, preparing, standardizing, and distributing the samples will necessitate the curtailment of other lines of established Bureau activities.

It is earnestly requested that all users of standard samples refrain from any unnecessary waste of the material, and that educational institutions limit their use strictly to primary standardization and to advanced research.

A list of the standard samples issued by the Bureau, together with charges and ordering and shipping regulations, is given in the Bureau of Standards *Supplement to Circular* 25, which will be sent upon application. In the future, standard samples will be issued only direct to users. This policy has been adopted to avoid, as far as possible, any chance of contamination or mixing of samples. Such chemical supply houses as have in the past carried a limited supply of certain standard samples for the accommodation of their customers can still render them service by remitting their orders with the proper fees to the Bureau for shipment.

RECENT RENEWALS—Sample 6*c*, a renewal of Iron D. Sample 25*a*, a renewal of the Manganese Ore 25, and Sample 42*a*, Melting Point Tin, have recently been renewed.

SAMPLES IN PREPARATION—Sample 45*a*, Melting Point Copper, and Sample 13*b*, a renewal of the 0.6C Basic Open Hearth Steel, will be issued on or before June 15. Sample 50, a new chrome (3.6 per cent)-tungsten (17.5 per cent)-vanadium (0.75 per cent) steel sample, will be issued on or before July 1. Sample No. 32*a*, a renewal of the chrome-nickel-steel, will be issued on or before August 1. Samples 23*a* 0.8C Bessemer Steel, and 51, a new 1.2C Electric Furnace Steel, will be issued on or before September 1. Sample No. 10*c*, a renewal of 0.4C Bessemer Steel, has been ordered and should be ready by October 1.

OBITUARY

GEORGE GILBERT POND

In the death of Dr. George Gilbert Pond, Professor of Chemistry and Dean of the School of Natural Science at the Pennsylvania State College, the chemical profession loses one of its most able and productive teachers. Although apparently in the best of health, he contracted pneumonia while on a business trip, and after an illness of but five days died in New Haven, Conn., on May 20.

George Gilbert Pond

Dean Pond was born at Holliston, Mass., March 29, 1861, and came from fine old New England stock. His father, Abel Pond, was a merchant of high standing in the community, and his mother was Amelia Robinson. After attending the Holliston High School he went to Amherst, from which college he graduated in 1881; the remainder of that year and the following he spent at the University of Göttingen. On his return from Germany Dr. Pond became instructor in chemistry at Amherst, where he remained until the summer of 1888, when he accepted the professorship of chemistry at the Pennsylvania State College. In 1896 he became dean of the newly created School of Natural Science.

Dean Pond found the Pennsylvania State College a struggling institution almost lost in the mountains of Pennsylvania. He left it a powerful university of three thousand men with a loyal group of alumni of great strength doing yeoman work throughout the country. While many factors contributed to the growth of the institution, none was more potent than the high standard of scholarship which it was soon obvious was to be maintained there. Of this moral and intellectual standard Dean Pond was the accepted exponent—a rock of rectitude which no emergency, however real, could move. His moral courage and high principles of action not only kept him from faltering when confronted with difficult situations, but were a positive force which upheld the hands and hearts of his colleagues.

As a teacher of great strength Dean Pond will be long remembered by his many students. A clear and exact expositor, he led the novice through the difficult paths of chemical philosophy into the glories of a great science. A constant inspiration and source of encouragement to those who worked, he was without consideration for the indolent or the wayward. He formed a worthy ideal of scientific accuracy and conscientious endeavor which was reflected throughout each one of his many lines of activity. Indeed the standard he set for himself was so high and he held himself to it with such rigorous exactness that he was often judged severe; and no doubt it was frequently difficult for him to appreciate the shortcomings and struggles of characters less lofty than his own. But under what sometimes appeared an austere and uncompromising exterior there beat a noble and generous heart; there existed an impelling desire to help anyone and everyone who exhibited the least inclination to help himself; there was present a sympathy, deep and broad and strong, that constantly flowed underneath his every action.

Dean Pond was a man of great physical and mental vigor, and worked with increased efficiency as the load became greater. During the recent protracted illness of the president of the College, Dean Pond carried his own teaching work, conducted the School of Natural Science, and, as acting president, performed the manifold duties of the executive office. But in addition to serving the college, he also served the community. The industries of the state are stronger for his having lived. Many a litigation has been expedited by the clarity and impartiality of his testimony. He held nothing in common with those "experts" who strive for triumph rather than for truth.

Dean Pond is gone; but his spirit lives on in those whom he has prepared by precept and by practice to "fear God, and take your own part." W. H. W.

WASHINGTON LETTER

By J. B. McDonnell, Union Trust Building, Washington, D. C.

The second session of the Sixty-sixth Congress came to an end on June 5 without taking final action on many measures of close interest to the chemical world.

As was forecast, the session ended with the peculiar deadlock over the dye bill in the Senate unbroken. Indications at the present time are that the dye people intend to stand by their guns and hold out for the full protection given by the committee bill.

A survey of the situation leads to the belief that either the fight will have to be resumed in December for the committee bill, or the dye men will have to wait until after March 4, next, when the new Congress will be convened and the country has given one party or the other greater leeway in the number of votes and, consequently, a stronger control of legislation.

The Democrats of the Senate will not accept the Moses amendment. They have already emphatically refused to do so and the same personnel will sit at the December session. That the House Democrats will refuse to accept such a tariff proposal, also is true. Adoption of the Moses amendment as the mainstay of the dye protective bill would simply mean that the support offered heretofore by the Democrats would be lost almost in its entirety.

Washington has seethed with politics recently. Some of those who have felt the dye bill did not receive the hearty support it should have from the Republican leaders are asking if there is possibly any connection between politics and the generalship employed by Senator Watson, of Indiana, in charge of the bill. Senator Moses, of New Hampshire, was one of the campaign managers of General Wood for the Republican nomination. Senator Watson, reports here say, is not having any too easy a time in his own state and is anxious to mend every one of his fences possible. The Indiana delegation declared for Wood. The Wood forces at the convention threw their strength to him and named him chairman of one of the most important committees of the convention.

Senator Wolcott, of Delaware, in a speech on the floor of the Senate, just before adjournment, took issue with statements made during the speech of Senator Thomas, of Colorado, with reference to the agreement entered into between the du Pont Company and Levinstein's, of England. The charges made by the Colorado senator, that the agreement was designed to create a monopoly and was an agreement between the two concerns not to compete with each other, Senator Wolcott declared were entirely unjustified by the facts. The agreement, Senator Wolcott continued, dealt solely with patents and secret processes owned and controlled by the concerns themselves and did not attempt to deal with any other dyestuffs, processes, or possible markets.

Following a very determined fight on the part of Senator Norris, of Nebraska, the Nolan-Norris bill providing for reorganization of the Patent Office here was sent to conference between the House and Senate during the last three days of the session. As passed by the Senate, the increased salaries provided for in the bill passed by the House were somewhat reduced. The measure will retain its parliamentary status and be ready for action by a conference committee when the Congress reconvenes in its next session.

A very important amendment attached to the bill was the Nolan-Norris bill providing for the acceptance by the Federal Trade Commission of patents and licensing manufacture under them. This bill, added as an amendment to the Patent Office reorganization measure, authorizes the Federal Trade Commission "to accept assignment of, or license or other rights or powers under, to develop, to issue or refuse to issue licenses under, to encourage the industrial use and application of" inventions, patents and patent rights on behalf of the United States, which may be tendered from time to time by government employees. Provisions which would permit anyone to assign patents to the Commission were changed before passage by the Senate. Use of patents assigned to the Government under the bill would be licensed for a fee to be paid into the Treasury of the United States. The inventor would be paid such portion of this fee as the President deemed just.

Creation of some machinery under which inventions, processes and patents developed by experts and others in the government employ could be turned over to the Government and controlled by it has been urged for some time. Hearings held on this bill before the House Patents Committee, however, developed some opposition to its form, Dr. Bernhard Hesse, representing the Manufacturing Chemists' Association and the General Chemical Company, appearing before the committee in opposition to the measure as drawn. E. C. Prindle, New York patent attorney, representing the association, also appeared.

This hearing was held prior to the attachment of the bill to the Patent Office reorganization measure in the Senate. Director of the Bureau of Mines Cottrell and Drs. Alsberg and Stewart, of the Bureau of Chemistry of the Department of Agriculture, together with Dr. Hesse and Mr. Prindle, were named informally as a committee to work out an agreement upon the points at issue by Representative Nolan, of California, author of the measure. Dr. Stewart has said that following conferences the differences between the two sides did not appear to be radical and he thought that a compromise could be reached without great difficulty.

Representative Nolan tried to get the measure up on the floor of the House the last of May but an objection made by Representative Gard, of Ohio, defeated the request. The bill now has passed the Senate in the form of the amendment as above outlined and goes to conference between the two Houses. It must wait, of course, until Congress reconvenes before any further action can be taken.

Referring to the bill during debate in the Senate, Senator Norris declared that it had "brought forth some objection not from inventors but from great corporations like the National Chemical Co., the great fertilizer trust, and others like that."

"To my mind," he continued, "it is of as much importance as the reorganization of the Patent Office itself. We have in the Government employ a large number of scientific men, in the Bureau of Standards, in the Bureau of Chemistry, in the Bureau of Mines, and perhaps some other bureaus. They are high-class men, wedded to their profession, particularly in the Bureau of Chemistry, which has excited so much interest during the war and since all over the world. They are continually making inventions and improvements. Scientific men all over the country are unanimously behind that."

Strong resentment is expressed against the report of the Graham committee of the House which investigated the Muscle Shoals nitrate plant in publicity matter which has been printed and distributed by the Air Nitrates Corporation. "It will take more mud than this to hide the real achievements at Muscle Shoals," it is declared in a statement sent out.

Dye investigations carried on by the color laboratory of the Bureau of Chemistry of the Department of Agriculture will be considerably reduced as a result of the cut in appropriations given by Congress, Secretary of Agriculture Meredith has pointed out in a public statement. "The appropriation for color investigations in the Bureau of Chemistry has been reduced by $30,020, or more than 30 per cent below the funds available this year," Secretary Meredith said. Work of the laboratory already has resulted in the granting of sixteen patents, he continued, and cited development of a process by which phthalic anhydride could be manufactured for 45 cents a pound as an example of the work done by the laboratory.

Discovery that the entire content of corn-cobs can be converted into useful products was cited by the Secretary as another example of the work of Department chemists. Furfural has been discovered as one of the by-products of corn-cobs, while other by-products include acetate of lime, from which acetic acid is made, cellulose, and an adhesive of exceptionally high quality.

An amendment to the third deficiency appropriation bill proposed by Senator Lodge, of Massachusetts, provides an appropriation of $2,500 for two officers of the Public Health Service to represent the United States at the Sixth International Sanitary Conference which is to be held at Montevideo, Uruguay, from December 12 to 20, 1920.

Suit against the Alien Property Custodian has been filed in the Supreme Court of the District of Columbia by Merck & Company, of New York City, a drug and chemical manufacturing concern. The suit, filed against the Alien Property Custodian and the Treasurer of the United States, is to recover $538,000, of which amount $490,000 represents a debt owed by the firm of E. Merck, drug and chemical manufacturers, Darmstadt, Germany. The Alien Property Custodian refused to make payment in the absence of the representatives of the concern in Germany.

The second questionnaire dealing with consumers' needs for German dyestuffs will be sent to consumers throughout the country in the near future. Some time ago the War Trade Board Section sent out a questionnaire to dye manufacturers relative to their needs for German intermediates.

Relief from the situation of having no funds to carry on its work after the end of the present fiscal year was granted the War Trade Board Section by the insertion in the sundry civil appropriation bill of an appropriation of $25,000 to carry on the work of the Board. With two representatives of the Board in Europe at the present time, the belief has been expressed that this sum is not sufficient to meet the needs for the next year.

Establishment of a chemical research laboratory was announced recently by George Washington University.

Along with the dye measure, bills which failed to pass through the legislative mill of Congress and which were pending when the session ended, included the laboratory glassware and scientific instrument tariff bill, bills dealing with fertilizers, government production of atmospheric nitrogen, stream pollution by chemicals, and a measure prohibiting exportation of helium.

June 14, 1920

INDUSTRIAL NOTES

The suit of the Dow Chemical Company *vs.* American Bromine Company and A. E. Schaefer, chemist of the American Company and formerly a chemist of the Dow Company, to restrain the American Bromine Company from operating its Midland plant in the recovery of bromine and the manufacture of bromides, and involving charges of using the trade secrets of the Dow Company, has been decided by the Michigan Supreme Court in favor of the American Bromine Company. Previous to the war, the Dow Company had a practical monopoly in Michigan and controlled the bromide market, but when the price of bromides rose enormously after the beginning of the war, the Emerson Drug Company of Baltimore and the Dr. Miles Remedy Company of Cincinnati, both large users of bromides, organized the American Bromine Company and began the manufacture of bromides at Midland. The charges of the Dow Chemical Company, brought more than two years ago, were sustained at that time in the Midland County Court, and an appeal was taken to the State Supreme Court, whose decision in the matter is final. That body has now reversed the decision of the County Court. The court's opinion is in part as follows:

> We are impressed that the claim of secrecy on the part of the plaintiff is an afterthought, indulged in, possibly, by reason of the fact that Mr. Dow felt that relief through injunction process from the Federal Courts for infringement was doubtful. We are of the opinion that the Schaefer patent, under which the corporate defendant is now operating, was, as claimed by him, based upon investigation and invention subsequent to the termination of his employment by plaintiff It is, therefore, not subject to the terms of the contract existing between him and the plaintiff during the latter years of his employment. If said patent is an infringement on any patent owned or controlled by plaintiff (as originally claimed by Mr. Dow), plaintiff has its remedy in the Federal courts for such infringement. Upon broad, equitable principles and in consideration of public policy, plaintiff should be denied relief unless its claim thereto is established beyond peradventure. After a careful consideration of this very voluminous record, we have no hesitation in reaching the conclusion that plaintiff has failed to so establish its right to relief. The bill is dismissed, with costs in both courts.

A committee has been appointed in France to take charge of the establishment in Paris of laboratories for chemical research, under the name "Institut de la Victoire." The committee is composed of representatives of French science, politics, and industry, and will work in close coöperation with government officials.

The Steel Company of Canada, Ltd., affiliated with the United States Steel Corporation, is installing a benzol plant in connection with its coke ovens. It is expected that 100,000 gal. of motor fuel per month will be turned out. Production is expected to begin in September.

Total exports of tanning materials from the United States during the month of April 1920 were valued at $278,461, according to the official figures of the Bureau of Foreign and Domestic Commerce. The countries receiving the largest amounts are as follows:

Belgium	$4,500
France	11,228
Italy	6,986
England	120,668
Canada	107,529
Cuba	4,960

Rosin and glycerol valued at $30,000 were destroyed by a recent fire at the storage yards of Procter and Gamble at Ivorydale, Ohio. The fire started from a spark from a locomotive and burned so fiercely that the firemen could do practically nothing to stop it. Trenches were dug around the fire, and all movable property carried from the danger zone.

The fertilizing plant of Armour and Company at Chicago was destroyed on May 24 by a fire which originated in an explosion of an ammonia tank. Damage estimated at $150,000 was caused and for a time a large section of the stock yards was threatened.

The United States Civil Service Commission has announced an examination for Research Engineer at $3,000 to $3,600 a year, to fill a vacancy at Watertown Arsenal, Watertown, Mass., and positions requiring similar qualifications. Requirements include graduation in metallurgical, mining or chemical engineering from a college of recognized standing, and at least eight years of experience in mining, metallurgy or allied work, at least four years of which must have involved experience in the handling of men. A reading knowledge of scientific French and German is also required. Theses, reports, and publications must be filed with application. Applications must be filed with Civil Service Commission, Washington, D. C., by July 20, 1920.

The Commission has also announced an examination for organic chemist and inorganic chemist (open to men only) to fill vacancies in the Philippine Service and similar positions, at $3,000 a year. Applicants must be college graduates with training and experience in organic and in inorganic chemistry. Applications must be filed with the Civil Service Commission, Washington, D. C., by July 6, 1920.

The Monsanto Chemical Works have recently announced their intention to begin the manufacture of synthetic camphor on a large scale. The plant is expected to be producing in quantity by the end of 1920. With the decreasing supply of Japanese camphor and the increasing demand, especially from the celluloid industry, the future of synthetic camphor looks very promising.

The Graesser Monsanto Chemical Works, Ltd., has been established in Great Britain, by an amalgamation of the British interests of Monsanto Chemical Works of St. Louis with R. Graesser, Ltd., of Ruabon, N. Wales. The new firm will begin manufacture in Ruabon of the full line of chemicals manufactured by the Monsanto Chemical Works in America, and will take over the London office for the handling of all European sales.

A Canadian Bureau of Scientific Research is to be established at an initial cost of $600,000 for site, building, and equipment, and $50,000 for the first year's salaries and upkeep. Standardization of all measures of length, volume, weight, etc., of all forms of energy and of scientific apparatus used in industry and the public service will be one of its main functions.

$250,000 damage was caused by a fire at the Frankford Works of The Barrett Company on May 19, 1920. One of the boiler houses was destroyed and the power plant temporarily crippled, but it is not expected to interfere seriously with the production of naphthalene.

Construction of the plant of the Atmospheric Nitrogen Company near Syracuse, N. Y., is about to begin. According to present plans, the first unit, which is to be completed in about a year at a cost of $2,000,000, will be only the beginning of the new industry. The first buildings to be erected will include process building, conversion building, gas producer, two large gas holders, service building and boiler house, all of the industrial type.

At a conference recently held in Manchester, England, it was decided to establish a British Chemical and Dyestuffs Traders' Association, to protect the interests of the merchants and to see that the distributing side of the chemical and dyestuffs industry receives proper recognition in departmental regulations.

The Dominion Bureau of Statistics of Canada has completed a preliminary report on the cocoa and chocolate industry in Canada during 1918. The total capital invested was $3,694,339, the total cost value of materials used was $3,835,479, and the total production value was $6,306,379.

During the three months ending March 31, 1920, the factory production of fats and oils in the United States (exclusive of refined oil and derivatives) was as follows:

	Pounds
Vegetable oils	605,285,917
Fish oils	4,211,336
Animal fats	455,897,306
Grease	89,767,212
TOTAL	1,155,161,771

PRODUCTION OF REFINED OILS

	Pounds
Cottonseed	357,572,013
Coconut	60,736,738
Peanut	12,748,195
Soy bean	38,393,120
Corn	24,745,843

The dye and chemical properties of the Ault & Wiborg Company have been sold to a syndicate representing the three principal dye works of Basle, Switzerland. An American corporation is to be formed to take over the operation of the works and the management will be in the hands of the Swiss interests. The Ault & Wiborg Company will retain a large interest in the new corporation, and Mr. Ault will be a director. New dye and chemical plants are planned, as well as enlargements of those already in operation. It is stipulated in the contract that no German money, directly or indirectly, shall ever be used in this industry. The Swiss companies interested are the Society of Chemical Industry, the Sandoz Chemical Works, and J. R. Geigy, S. A.

Trustees of Dartmouth College have announced the construction of a new $350,000 chemical laboratory.

Rules and regulations for the leasing of phosphate deposits in the public lands have just been approved by Secretary of the Interior Payne. About 2,500,000 acres of land in Wyoming, Idaho, Utah, and Montana for a number of years have been awaiting legislation recently enacted by Congress. They will now be open to lease in areas not exceeding 2,560 acres each, and should add largely to the fertilizer supply of the United States. Applications for leases are to be filed with the local land offices for transmission to the Secretary of the Interior.

The Federal Trade Commission has cited the United Indigo & Chemical Co., Ltd., of Boston, engaged in the manufacture and sale of dyestuffs, chemicals, etc., in formal complaint of unfair competition. The company is charged with secretly giving cash commissions and other rewards to employees of its customers and its competitors' customers to induce the purchase of its products.

The progress of the French chemical industry due to the effort made during the war is shown by the following table of production:

	1913 Tons	1920 Tons
Sulfuric acid	850,000	1,700,000
Nitric acid	20,000	300,000
Oleum	6,000	200,000
Liquid chlorine	none	18,000
Bromine	none	500
Synthetic nitrates	none	250,000
Phosphorus	300	3,000

The zinc oxide plant of the Empire Zinc Co., Canon City, Col., is nearing completion and ores are now being roasted, preparatory to actual production of the zinc oxide. The plant is modeled along the lines of the plants of the New Jersey Zinc Co., of which the Empire Zinc Company is a subsidiary, and the same grade of zinc oxide will be produced. The plant is expected to become an important unit in the New Jersey Zinc Company's operations, and has been built with a view to future extensive additions.

To protect aluminum and aluminum alloys from corrosion, L. von Grotthuss has tried browning the metal electrolytically. The aluminum is suspended in an electrolyte consisting of a sulfur compound of molybdenum with a zinc anode at a temperature of 60° to 65° C. The aluminum is soon covered with a dark brown coating and may be bent or rolled without cracking the coating. Aluminum thus treated was immersed in a salt solution for two months without showing the slightest trace of corrosion.

PERSONAL NOTES

The council of the Society of Chemical Industry awarded its medal for the year 1920 to **Monsieur Paul Kestner**, first president of the Société de Chimie Industrielle of France, in recognition of his distinguished services to the chemical industry.

Mr. L. W. Haskell, vice president of the Southern Cotton Oil Co., died at his home in Savannah, Ga., on June 4, 1920.

The honorary degree of doctor of laws was conferred upon **Dr. William H. Nichols** at the recent commencement exercises of New York University.

Mr. Henry H. Mayers has left E. I. du Pont de Nemours & Co., Paulsboro, N. J., where he was employed as supervisor of the strontium nitrate department, to accept a position in the research department of Rohm & Haas Co., Bristol, Pa.

Mr. Leroy M. Law, formerly chief chemist of the Interocean Oil Co., New York and Baltimore, announces his association with the New Orleans Refining Co., New York City.

Mr. R. W. Ruprecht, formerly chemist and superintendent of the fertilizer factory of F. W. Tunnell & Co., Inc., of Philadelphia, has been appointed chemist of the Florida Experiment Station, Gainesville, Fla.

Mr. E. Wurgler, for many years assayer and chemist at various plants of the American Smelting and Refining Company, and recently chief chemist at their Durango Plant, resigned his position with that firm to enter business with Oscar J. Frost, assayer, Denver, Colo.

Mr. Robert V. Townend resigned his position as chemist in charge of the chlorinated toluene products with the Semet-Solvay Co., Syracuse, N. Y., to accept a position with the Victor Talking Machine Co., Camden, N. J., where he will organize and direct their department of chemical research. Up until the time Mr. Townend left Syracuse, he served as secretary of the Syracuse Section of the American Chemical Society.

Mr. W. N. Pritchard, Jr., is now doing research work on dyes for the Calco Chemical Co., Bound Brook, N. J., having formerly been with Procter and Gamble at Augusta, Ga., as superintendent of a pulp mill.

Mr. Howard Stoertz, formerly analytical and experimental chemist at the Harrison Works of E. I. du Pont de Nemours & Company, is now research chemist for the Crown Cork and Seal Co., Baltimore, Md.

Mr. Allen H. Lloyd resigned his position in the St. Louis Meat Inspection Laboratory of the U. S. Department of Agriculture to accept a position in the Commercial Laboratories at Indianapolis, Ind.

Mr. Peter J. Waldstein, formerly chief chemist for John Lucas and Co., Inc., Philadelphia, Pa., is employed at present in a similar capacity with the Continental Varnish Co., Brooklyn, N. Y.

Mr. Kenneth E. Bell has resigned his position as research associate with the research laboratory of applied chemistry, Massachusetts Institute of Technology, to accept one as chemical engineer with the Lewis Recovery Corporation, Boston, Mass.

Dr. Marston T. Bogert, professor of chemistry at Columbia University, New York City, was recently named a member of the Tariff Commission by President Wilson. Dr. Bogert was elected president of the American Section of the Société de Chimie Industrielle of France, at its recent meeting.

Mr. G. W. Morey, of the Geophysical Laboratory, Carnegie Institution of Washington, who has been on leave of absence and in charge of the optical glass plant of the Spencer Lens Company of Buffalo, N. Y., since November 1918, recently returned to resume his research work at the Laboratory.

The University of North Carolina chapter of Sigma Xi was installed May 26 by **Prof. C. E. McClung**, of the University of Pennsylvania, president of Sigma Xi. The charter members of the North Carolina chapter are **Drs. James M. Bell** and **Joseph Hyde Pratt**, initiated at Cornell and Yale, respectively, and **Drs. F. P. Venable, H. V. Wilson, W. D. MacNider, A. S. Wheeler, W. C. Coker** and **William Cain**, all members of the faculty.

Mr. Clarence W. Holmes has left the employ of the Weirton Steel Co., Wierton, W. Va., to become laboratory assistant at the Universal Steel Co., Bridgeville, Pa.

Mr. R. G. Gutelius has left the experimental laboratory of the Atlas Powder Co., Stamford, Conn., and is in the experimental laboratory of the Aetna Explosives Co., at Emporium, Pa.

Dr. F. H. Rhodes has resigned as director of research for the chemical department of The Barrett Company, Frankford, Pa., in order to accept the appointment as professor of industrial chemistry in Cornell University.

Mr. H. D. Grigsby has resigned from the provisions and clothing department of the Navy where he was in charge of the Inspection Laboratory, and is taking a position as research chemist with the Ward Baking Company at their Bronx Plant, New York City.

Mr. C. E. Herring was named First Assistant Director of the Bureau of Foreign and Domestic Commerce, and **Mr. O. P. Hopkins**, Second Assistant Director of the Bureau, in nominations sent to the Senate May 27 by President Wilson.

The National Research Council has elected the following officers for the year beginning July 1, 1920: Chairman, **H. A. Bumstead**, professor of physics and director of the Sloane Physical Laboratory, Yale University; First Vice Chairman, **C. D. Walcott**, president of the National Academy of Sciences and Secretary of the Smithsonian Institution; Second Vice Chairman, **Gano Dunn**, president of the J. G. White Engineering Corporation, New York; Third Vice Chairman, **R. A. Millikan**, professor of physics, University of Chicago; permanent secretary, **Vernon Kellogg**, professor of biology, Stanford University; Treasurer, **F. L. Ransome**, treasurer of the National Academy of Sciences.

Mr. C. H. McClure has severed his connections with the Commonwealth Edison Co., where he was employed as chief chemist, and has accepted a position as chemist with the Menasha Printing and Carton Co., Menasha, Wis.

Mr. Kenneth P. Monroe has resigned as chemist in the color laboratory, U. S. Bureau of Chemistry, Washington, D. C., to accept a research position in the Jackson Laboratory of E. I. du Pont de Nemours & Co., Wilmington, Del.

Dr. George D. Van Epps, formerly connected with the Citro Chemical Co., Maywood, N. J., has returned to the Continental Motors Corp., Muskegon, Mich., in his former capacity as analytical and research chemist.

Mr. George K. Senior has left the American Textile Soap Co., Springfield, Mass., where he was employed as chemist, to take a similar position with the Warren Soap Manufacturing Co., Boston, Mass.

Mr. Henry Sohn, formerly with the Sanitary District of Chicago, as assistant chemist, has accepted the position of assistant bacteriologist at the Cincinnati Water Works, California, Ohio.

Mr. Asher F. Shupp recently resigned his research fellowship at the Mellon Institute of Industrial Research to become chief chemist to the Faultless Rubber Co., Ashland, Ohio.

Mr. Shreve Clark, formerly chemist and assistant testing engineer to the State Highway Department of Ohio, Ohio State University, Columbus, O., recently became testing engineer to the State Highway Department of Virginia, Virginia Polytechnic Institute, Blacksburg, Va. In addition to his regular duties in the Highway Department, Mr. Clark will instruct a class of senior civil engineers on highway materials.

Mr. Frank E. Glassman has severed his relations with the Specials Chemical Co., Highland Park, Ill., and has organized the Vulcan Chemical Co., Chicago, Ill., which firm will manufacture a complete line of soldering compounds for the electrical and automobile industries.

Mr. E. F. Berger, formerly assistant chemist at the Michigan Agricultural College Experiment Station, is at present connected with the Patton Paint Co., Milwaukee, Wis., as chemist in the insecticide plant.

Mr. Robert G. O'Kane, previously engaged with the Brown Company on certain special electrochemical investigations, has become an executive on the operating staff of the Carrollville, Wis., plant of the Newport Company.

Mr. Raymond E. Whitney has left the employ of the Monsanto Chemical Works, E. St. Louis plant, to accept a position as chemist of the ammonia leaching and allied processes plant of the Calumet and Hecla Mining Co., Lake Linden, Mich.

Dr. H. R. Kraybill has left the Bureau of Plant Industry, U. S. Department of Agriculture, where he was assistant physiologist, and has been appointed professor of agricultural chemistry and head of the department of chemistry in the Experiment Station of New Hampshire State College, Durham, N. H.

GOVERNMENT PUBLICATIONS

By Nellie A. Parkinson, Bureau of Chemistry, Washington, D. C.

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

CONGRESSIONAL COMMITTEES

Nitrogen. Production of atmospheric nitrogen, hearing on S. 3390, to provide further for national defense, to establish self-sustaining federal agency for manufacture, production, and development of products of atmospheric nitrogen for military, experimental, and other purposes, to provide research laboratories and experimental plants for the development of fixed-nitrogen production, and for other purposes. 104 pp. 1920.

Zinc. Senate Report 511. 3 pp. April 9, 1920. Production of zinc ores, report to accompany H. R. 6238 (to provide revenue for the Government and to establish and maintain production of zinc ores and manufactures thereof in the United States); submitted by Mr. Watson.

GEOLOGICAL SURVEY

Lead in 1917. General Report. C. E. Siebenthal. Separate from Mineral Resources of the United States, 1917, Part I. 17 pp. Issued May 8, 1920. The output of refined lead in the United States from domestic ores in 1917 was 548,450 short tons, valued at $94,333,000, at the average sales price of refined lead, compared with 552,228 tons, valued at $76,207,000 based on the average "outside" spot quotation at New York in 1916—a loss in quantity of 3,778 tons, or nearly 1 per cent, and a gain in value of $18,126,000, or nearly 24 per cent.

Anticlines near Maverick Springs, Fremont County, Wyoming. A. J. Collier. Contributions to Economic Geology, 1919, Part II. 18 pp. Issued April 26, 1920. The oil produced in this district is a heavy asphaltic dark brown oil, having an odor of hydrogen sulfide.

Geology of Alamosa Creek Valley, Socorro County, New Mexico, with Special Reference to the Occurrence of Oil and Gas. D. E. Winchester. Contributions to Economic Geology, 1920, Part II. 15 pp. Bulletin 716-A. Issued May 12, 1920.

The Upton-Thornton Oil Field, Wyoming. E. T. Hancock. Contributions to Economic Geology, 1920, Part II. 18 pp. Bulletin 716-B. Issued April 29, 1920.

Mineral Resources of the United States 1917. Part II. Non-metals. G. F. Loughlin. 1293 pp. Cloth bound. 1920. The chapters covered by this report are: fuel briquetting; strontium; phosphate rock; sulfur, pyrites, and sulfuric acid; magnesite; talc and soapstone; gypsum; graphite; slate; feldspar; gems and precious stones; salt, bromine, and calcium chloride; mica; asbestos; sand-lime brick; silica; abrasive materials; asphalt, related bitumens, and bituminous rock; fuller's earth; peat; barytes and barium products; fluorspar and cryolite; sodium salts; cement; sand and gravel; potash; mineral waters; clay-working industries; lime; stone; petroleum; coal (Part A), production; natural gas; gasoline from natural gas; coke and by-products in 1916 and 1917; coal (Part B), distribution and consumption. These separate chapters have previously been reviewed.

Chromite in 1918. J. S. Diller. With Papers on Foreign Deposits of Chromite by E. F. Bliss and H. R. Aldrich, and on Chromite and Chromiferous Iron Ore in Cuba by E. F. Burchard. Separate from Mineral Resources of the United States, 1918, Part I. 69 pp. Published May 15, 1920. The year 1918 was the most eventful in the history of chromite. The domestic production was by far the largest in the history of the country and demonstrated that when necessary the United States can, at least for a few years, supply its own chromite. The total quantity of chromite of all grades mined and shipped in the United States in 1918 was 82,430 long tons (92,322 short tons), valued at $3,955,567.

BUREAU OF MINES

Monthly Statement of Coal-Mine Fatalities in the United States, February 1920. W. W. Adams. 10 pp. Paper, 5 cents. April 1920.

Procedure for Establishing a List of Permissible Gas Masks; Fees, Character of Tests, and Conditions under Which Gas Masks Will Be Tested. Supplement to Schedule 14. 4 pp. 1920.

Approved Explosion-Proof Coal-Cutting Equipment. L. C. Ilsley and E. J. Gleim. Bulletin 78. 53 pp. Paper, 25 cents. 1920. The first part of the bulletin deals with the general theory of protection from fire damp, gives the schedule of the Bureau of Mines, and shows its application to the testing of commercial apparatus. The second part covers a detailed description of the apparatus that has been tested and approved under this schedule, together with a resumé of the tests on which the approvals were based.

Coal-Mine Fatalities in the United States, 1919, and Coal-Mine Statistics Supplementing Those Published in Bulletin 115. List of Permissible Explosives, Lamps, and Motors Tested prior to January 31, 1920. A. H. Fay. Bulletin 196. 86 pp. Paper, 15 cents.

The Determination of Mercury. C. M. Bouton and L. H. Duschak. Technical Paper 227. 44 pp. Paper, 10 cents. 1920. The method described in this report was developed by the Bureau of Mines for use in a study of mercury condenser losses. Illustrations are given, showing the apparatus employed. A bibliography on analytical methods for the determination of mercury is also included.

Accident Prevention in the Mines of Butte, Montana. Technical Paper 229. Covers safety organization and work of Butte mining companies, etc. Paper, 10 cents. Issued June 1920.

Development of Liquid Oxygen Explosives during the War. Technical Paper 243. Paper, 10 cents. Issued June 1920. Covers historical review, Bureau of Mines experiments, recent German development of liquid oxygen explosives, European observations of bureau representatives, summary and conclusions regarding liquid oxygen explosives, including blasting, equipment, safety precautions, etc.

Quarry Accidents in the United States during the Calendar Year 1918. A. H. Fay. Technical Paper 245. 52 pp. Paper, 10 cents. April 1920.

Perforated Casing and Screen Pipe in Oil Wells. E. W. Wagy. Technical Paper 247. Petroleum Technology 55. 48 pp. Paper, 20 cents. Issued April 1920.

Effect of Gasoline Removal on the Heating Value of Natural Gas. Technical Paper 253. Paper, 5 cents. Issued June 1920. Covers a review of the situation, character of natural gas examined, advantages of gasoline plants, and experimental results in laboratories.

BUREAU OF STANDARDS

Recommended Specification for Iron-Oxide and Iron-Hydroxide Paints. Circular 93. 8 pp. Issued April 21, 1920. Prepared and Recommended by the United States Interdepartmental Committee on Paint Specification and Standardization, March 22, 1920. Outlines general specifications for the pigment, liquid, semi-paste, and ready-mixed paint, methods of sampling and analysis, and describes the reagents to be used in examining these products.

Recommended Specification for Black Paint, Semi-paste and Ready-mixed. Circular 94. 8 pp. Issued April 21, 1920. Prepared and recommended by the United States Interdepartmental Committee on Paint Specification and Standardization, March 22, 1920. Outlines general specifications for the pigment, liquid, semi-paste, and ready-mixed paint, methods of sampling and analysis, and describes the reagents to be used in examining these products.

Weights and Measures. Miscellaneous Publication 41. 226 pp. Paper, 20 cents. 1920. This is a report of the twelfth annual conference on weights and measures of the United States held at the Bureau of Standards, Washington, D. C., May 21 to 24, 1919.

DEPARTMENT OF AGRICULTURE

Saponified Cresol Solutions. J. M. Schaeffer. Department Bulletin 855. This paper describes a series of experiments undertaken with the object of preparing a saponified cresol solution which would be cheaper and at the same time no less effective as a disinfectant than those at present in use.

Insect Powder. C. C. McDonnell, R. C. Roark and G. L. Keenan. Department Bulletin 824. 100 pp. Paper, 20 cents. Issued June 3, 1920.

Articles from the Journal of Agricultural Research

Effect of Calcium Sulfate on the Solubility of Soils. M. M. McCool and C. E. Millar. 19 (April 15, 1920), 47–54.

Effect of Reaction of Solution on Germination of Seeds and on Growth of Seedlings. 19 (April 15, 1920), 73–95.

COMMERCE DEPARTMENT

Commerce. Schedule governing statistical classification of imports into the United States, with rates of duty, and regulations governing the preparation of monthly and quarterly statements of imports and monthly statement of exports of foreign commodities; approved June 10, 1918. Edition of 1920. Foreign and Domestic Commerce Bureau. Supersedes and combines Schedules A and E. 98 pp. Paper, 10 cents.

UNITED STATES TARIFF COMMISSION

Incandescent Gas-Mantle Industry. Its raw materials and by-products, monazite sand, thorium and cerium nitrates, pyrophoric alloys, and mesothorium. Tariff Information Series 14. 32 pp. Paper, 5 cents. 1920.

FEDERAL BOARD FOR VOCATIONAL EDUCATION

Industrial Accidents and Their Prevention. R. R. Ray. Bulletin 47. Employment Management Series 7. 66 pp. 1920.

NAVY DEPARTMENT

Lubricating Oils as Purchased by Bureau of Steam Engineering. General information for refiners of petroleum regarding tests of lubricating oils at Engineering Experiment Station, Annapolis, Md., also information concerning tests of greases and soluble oils at laboratory of Machine Division, Navy Yard, New York. Revised March 1, 1920. 32 pp.

TREASURY DEPARTMENT

Denatured Alcohol. Regulation 61 relative to production, tax payment, etc., of industrial alcohol, and to manufacture, sale, and use of denatured alcohol under Title 3 of national prohibition act of October 28, 1919. Treasury Decision 2986 (supplement to Treasury Decision 38, No. 10). 107 pp. Paper, 10 cents. 1920.

UNITED STATES PUBLIC HEALTH SERVICE

A Further Study of the Excess Oxygen Method for the Determination of the Biochemical Oxygen Demand of Sewage and Industrial Wastes. E. J. Theriault. 35, 1087–97.

COMMERCE REPORTS—MAY 1920

A report has been prepared showing the development of the **sandalwood oil** industry in India, and the distribution of this trade in previous years. (P. 651)

England has received her first **reparation dyestuffs** from Germany. (P. 677)

The successful cultivation of **camphor** within the British Empire is no longer doubtful. (Pp. 692–3)

There is a steady demand in Japan for **soda ash, caustic soda, bicarbonate of soda, carbolic acid** (phenol), **boric acid, borate of soda, bichromate of potash,** and **rosin,** for most of which the United States is the principal source of supply. (P. 694)

The effectiveness of the Japanese **camphor** monopoly for increased production is shown by the production in 1919 being almost double the amount produced in 1918. (P. 694)

A description is given of the **extraction of tannin** from the Indian myrobalans. (Pp. 713–5)

Chicle-producing trees have been discovered in British Guiana. (P. 716)

The suggestion that the forestial riches of Argentina be utilized for the manufacture of **paper pulp** is meeting with favor. (Pp. 716–7)

Statistics are given showing the production of the leading Burma **rubber** plantations and the exportation of rubber for the past five years. (P. 727)

Final returns covering the exportation of **tin** from Hongkong in 1919 indicate a disastrous year. (Pp. 743)

Statistics are given showing the imports of **aniline** and **alizarin** into Madras by countries for five years. (P. 745)

The total French imports of **crude rubber** for 1919 were 32,455 metric tons against 19,927 tons in 1918. (P. 745)

Great progress has been made in the revival of the Indian **indigo** industry. (Pp. 746–7)

The imports of **chemicals** into Burma during the year ended March 31, 1918, showed a considerable increase over the four years immediately preceding. (P. 758)

There is a considerable movement of **paraffin** into and out of Hongkong. In 1918 the United States furnished wax to the extent of 59 per cent of the total, but in 1919 furnished but 7 per cent, and that only in the last quarter of the year. (P. 767)

The **artificial silk** establishments of Belgium are employing 90 per cent of their 1914 personnel, but the production is slightly below 32 per cent of the pre-war figure. (P. 798)

The British Government has made arrangements to deliver to the Belgian zinc industry 240,000 tons of **zinc ore** within the maximum limit of two years. (P. 798)

The **mineral** resources of Armenia have been hardly explored or are impossible to exploit on account of the scarcity of available roads. The deposits of copper are innumerable. (P. 807)

Hull is now without doubt the largest **vegetable oil** center in Europe. During January and February 596,939 gal. of linseed oil, valued at $999,770, were invoiced through Hull for shipment to the United States. The outlook of the industry for 1920 is very promising. (Pp. 818–23)

A more or less acute shortage of **paper** is reported in Hongkong, Shanghai, and North China ports. (P. 823)

The utilization of Irish **mineral** resources is suggested. Accurate explorations will have to be made, however, before the practicability of reopening old mines and exploiting new fields is determined. (Pp. 828–30)

The export of **sulfur** from Sicily in 1919 amounted to 147,286 tons, as compared with 231,390 tons in 1918, but is still below the pre-war figures. There were no sulfur exports to the United States during 1919. (P. 835)

German war-time experiments showed that the distillation of **lignite** at a high temperature gave a liquid coal tar which contained certain ingredients suitable as a substitute for gasoline, kerosene, and lubricating oils. (P. 835)

The manufacture of **paper pulp from seaweed** is proving to be a profitable undertaking in Japan. (P. 836)

In spite of the heavy duty imposed on **toilet soaps** imported into Japan the importations of perfumed soaps increased from 105,000 lbs., valued at $39,000, in 1917 to 125,000 lbs., valued at $61,000, in 1918 and jumped to 387,000 lbs., valued at $184,000, in 1919. The demand for laundry soap is largely met by local production. (Pp. 836–7)

Norway in 1916 mined 29,398 short tons of **copper ore** and in 1917, 43,318 tons. During the same period the production of copper pyrites was 325,571 and 362,323 short tons, respectively. (P. 837)

Germany is to pay Switzerland 11,000,000 Swiss francs in order to cancel her war-time contract for the purchase of **aluminum** in Switzerland. (P. 854)

The German delivery of **chemicals** is so uncertain that Switzerland finds it practically impossible to carry on any satisfactory business with Germany. Chemical products from the United States can be purchased in Switzerland at a lower price in many instances than German houses are quoting. (P. 881)

The duties on **coal-tar dyes** imported into Spain have been fixed for a period of ten years at greatly increased rates. (P. 891)

The French **iron** and **steel** industry is reviewed. (Pp. 902–17)

A new **petroleum** deposit was recently discovered at Pechelbronn. New refineries are to be installed capable of distilling 73,000 tons of crude petroleum per year. The distillation is to be by the "continuous" process, with perfect vacuum. (P. 918)

The effect of the war on the Spanish **iron** and **steel** industry, one of the most important Spanish industries, is noted. (Pp. 934–44)

There is a great demand in Norway for **cellulose,** as well as **wood pulp** and **paper.** Since the armistice the sale of bleached sulfite has been greater than that of paper and sulfate cellulose. (P. 978)

The total shipments of **crude rubber** from the ports of Para, Manaos, and Itacoatiara, Brazil, and Iquitos, Peru, during the month of January 1920 amounted to 6,273,039 lbs. as compared with 6,624,915 lbs. in the corresponding month of last year. (P. 981)

Work on the erection of a **paper** and **pulp mill** in Newfoundland is to be started this month. The pulp and paper produced will be exported to England and the United States. (P. 991)

Previous to 1916 no **manganese** was mined in Costa Rica. Since that time production has steadily increased until in 1919 7,851.5 tons were exported. (P. 998)

American interests recently acquired the rights to three Bolivian **tin mines.** (Pp. 998–9)

The importation of **soda** and **soda ash** into Japan has greatly increased, and from 70 to 80 per cent of these imports come from the United States. (P. 1002)

German **shale** and **peat** have been suggested as substitutes for coal. (P. 1013)

It is reported that work is about to be resumed in the old Orijarvi **copper** and **zinc** mines in Finland. (Pp. 1018–9)

The French Minister of Finance has given notice that the price of **alcohol** distilled from **sugar beets** during 1920–1 will be based on the average price of No. 3 white sugar during November and December 1919. (P. 1043)

The manufacture of by-products from second-grade **coal** in South Africa is about to be commenced. A carbide and by-products plant is now in the course of construction. The seams of this second-grade coal are very thick, and consequently the raw material is easily obtainable. Tests show that the coal is high in nitrogen, and yields over 120 lbs. of sulfate of ammonia, 2.5 gal. of benzol, and 16 gal. of tar oil per ton of coal. (P. 1048)

An enterprising American has secured from the Italian government a concession for the utilization of 800 horse power of the waterfalls at Terni, and maintains that he can turn out nitrogenous plant food for the Italian farmer at a cost as low as 1 lira per kilo. The process has passed beyond the experimental stage and ammonia from this plant has already been put upon the market on a paying basis. (Pp. 1058–9)

The new import duties on **drugs** and **chemicals** in Uruguay affect 1,244 items and, in many cases, greatly increase the duties. (P. 1073)

Mexican **potassium nitrate,** in lots of from 30 to 100 tons per month, may be obtained. (P. 1076)

To ameliorate the serious situation caused by the shortage in France of **superphosphates** for agricultural purposes, the Under Secretary for the Merchant Marine has placed at the disposition of a group of manufacturers of this vitally necessary fertilizing material 35,000 tons of shipping, in addition to 6,000 tons already furnished, to be employed in the transportation of phosphate rock from Northern Africa. (P. 1087)

The Australian restrictions on the importation and exportation of **copra** have been removed. (P. 1089)

The **nitrate industry** of Chile is reviewed. (Pp. 1093–1103)

The lead and **zinc industry in Japan** is reviewed. (P. 1108)

There has been a fall in the prices of **tallow** in Great Britain (P. 1112)

An acute **scarcity** of **manganese ore** is reported in Great Britain, which greatly hinders the furnaces making ferromanganese. (Pp. 1112–3)

The Australian import prohibition on **dyes** is still effective. (P. 1121)

The British Water Power Resources Committee has a scheme for the utilization of the **water power** of the United Kingdom in place of coal and oil. (P. 1157)

An increase in the exportation of nearly all kinds of **vegetable oils** from the Mukden consular district of China is reported. (P. 1178)

The Spanish **olive oil** yield in 1919 amounted to 336,393 metric tons, compared with 255,202 tons in 1918, and 427,838 tons in 1917. (P. 1189)

The trade in **chemicals** at Hongkong in 1919 showed little life and very little increase over that of 1918, when it was difficult to secure supplies in any line. Importers found it difficult to secure supplies from the United States and most of them returned to their old British connections as rapidly as conditions permitted (P. 1197)

Rich veins of **mica** have been explored and are now being exploited in the district of Mehedintz, Rumania. (P. 1227)

SPECIAL SUPPLEMENTS ISSUED

UNITED KINGDOM—*22c*
SCOTLAND—*22d*
ARGENTINA—*41a*
BRAZIL—*43a*
COLOMBIA—*45a*
ADEN—*52a*
DUTCH EAST INDIES—*56a*

STATISTICS OF EXPORTS TO THE UNITED STATES

BURMA—(P. 733)
Paraffin wax

CHILE—(P. 1099)
Nitrate

SICILY—(P. 771)
Essence of bergamot

BOOK REVIEWS

The Condensed Chemical Dictionary. Second Printing, Corrected. The Chemical Catalog Co., Inc. 1 Madison Ave., New York. Price, $5.00.

A number of the errors to which attention was called in the review of the first printing [THIS JOURNAL, 12 (1920), 102] have now been corrected. In particular the editors state that the physical constants have been checked and are believed to be correct with the exception of the following typographical errors: (1) the boiling point of methyl chloride should be —23.73° instead of 23.73°, (2) the melting point of dinitrobenzene (para-) should be 172–173° instead of 372–373°.

AUSTIN M. PATTERSON

Manual of Industrial Chemistry. Edited by ALLEN ROGERS in collaboration with others. 3rd Edition thoroughly revised and enlarged. D. Van Nostrand Co., New York, 1920. Price, $7,50, net.

The third edition of this Manual of Industrial Chemistry comes from the press as a volume of over 1200 pages, an increase of more than 200 pages over the second edition issued in 1915. The book is however no more bulky than its predecessor. The success of the earlier editions is attested by the statement that this is the twelfth thousand printed. Almost every chapter shows revision and in many cases expansion. The first chapter on General Processes, by Professor Rogers himself, is much improved by expansion from 32 to 48 pages. The second chapter on Water for Industrial Purposes, written in the early editions by Mr. R. B. Dole, now deceased, has been rewritten by Messrs. Stabler and Chambers of the Geological Survey and expanded to cover 54 instead of 31 pages, presenting a very excellent treatment of the subject. The excellent chapter on Illuminating Gas by Mr. W. H. Fulweiler is increased from 63 to 82 pages. Other chapters show less expansion. Four new chapters are added, one of 12 pages on Turpentine and Rosin by Dr. Chas. H. Herty; one of 18 pages by Mr. Jerome Alexander on Colloids; one of 15 pages by Mr. Clarence V. Ekroth on Dehydrated, Dried, and Evaporated Foods, Condensed Foods; one of 27 pages on Baking by Mr. Arnold Wahl.

This book has the advantages and disadvantages which are inherent in such a collaborative effort. The writers are specialists in their subjects and errors of fact are few, but there is some duplication and considerable unevenness of treatment. The Industrial Chemistry of Carbon Compounds takes nearly two-thirds of the book and yet there is practically nothing on the manufacture of intermediates or dyes Paper manufacture is compressed to 15 pages and rubber to 24 pages, but the subjects of paint, varnish, and their raw materials are given nine chapters with a total of 105 pages. In contrast to this we find in the Inorganic Industry the metallurgy of iron and steel, treated, it is true, by a master, Bradley Stoughton, compressed to 17 pages; the industry of clay, bricks, and pottery cut to 7 pages, and the metallurgy of the non-ferrous metals touched on only casually in the chapter on Elements and Compounds.

The Electrolytic Decomposition of Sodium Chloride is given a separate chapter but the industries of evaporation and separation of salts in solution are given inadequate treatment. Common salt and the evaporation of brine are, it is true, given 5 pages, but the treatment is indiscriminating and statistics used in the 1915 edition and dating from 1912 have been carried forward without revision. Potash salts and the manufacture of soda ash receive only scanty and casual treatment in the chapter on Elements and Compounds.

The treatment of the various chapters is mainly descriptive. The increase in our theoretical knowledge is making it increasingly possible to show the reasons for technical success or failure and the limitations of processes. It is hoped that more emphasis may be placed on this aspect in future editions.

Those of us who recall how books like Lunge's "Sulphuric Acid and Alkali," and Allen's "Commercial Organic Analyses" have grown with successive editions may hope that the demand for this work will soon cause it to be issued in several volumes where the inorganic subjects and the theoretical treatment may have more generous recognition. However, in its present form, the book may be rated as the best single volume treatment of industrial chemistry in the English language.

ALFRED H. WHITE

From Newton to Einstein. By BENJAMIN HARROW, PH.D. 74 pp. D. Van Nostrand Co. New York: 1920. Price, $1.00.

This is a small but popular brochure rather than a book and has no doubt sprung out of the opportunism brought about by the popular furore over Einstein and his postulates. The first portion of the book is taken up with a general resumé concerning Newton and his law of gravitation and laws of motion together with his theory of light. Another small chapter deals with the ordinarily accepted, modern theory of light, and a final chapter treats of Einstein's theories and conceptions of the nature of light, and a statement of the observations and results of the astronomical experiments to watch the solar eclipse of May 1919, as far as its bearings on the Einstein theory are concerned. The author is thoroughly convinced of the naïveté of his readers, for in discussing the theory of light, when the term "ether" is mentioned, he assures us in a footnote that this is in no way connected with the well-known anesthetic.

The treatment of the subject is very similar to that in the various "special articles" which have from time to time appeared in the daily newspapers or in the magazine sections of the Sunday editions, concerning Einstein and his theories. Great stress is laid in this review of the work of Einstein in respect to its connection with the conception of light, and the popular sensationalism is catered to by claiming that the startling result of Einstein's discoveries is that light does not travel in a straight line as formerly supposed, but in curves, and consequently, notwithstanding the postulates of Euclid, two parallel lines probably meet long before finity is reached. Of course it is a sensational bit of news to announce to the trusting public that by the wonderful discovery of Einstein the whole conception of geometrical propositions has been proved false, but, as a matter of fact, the physical behavior or the physical nature of a ray of light has nothing whatever to do with the propositions and conceptions of pure mathematics or of geometry. But then perhaps, unless this type of newspaper sensationalism is resorted to, very little popular interest would be aroused in a scientific discussion which really involves very abstruse mathematical propositions.

The author also dabbles a little in the fourth dimension but has the good sense to state that the layman cannot grasp the meaning of the fourth dimension, although the mathematician can play with it in mathematical terms. The same might also be stated as being true of such mathematical toys as imaginary quantities. The square root of minus one, for example, is a plaything with which the mathematician can amuse himself in a variety of different ways, although the layman cannot have the slightest notion of its meaning, nor, in fact, can the mathematician himself, although some time he can use it with very good and practical results as a term in a mathematical series.

This little book of Dr. Harrow's no doubt will prove instructive and entertaining to the unscientific layman who has to be warned that the ether of the outside space cannot be used as an anesthetic, but there does not seem to be anything of interest in this publication for the scientist or the scholar.

J. MERRITT MATTHEWS

NEW PUBLICATIONS

By Clara M. Guppy, Librarian, Mellon Institute of Industrial Research, Pittsburgh

Aluminum: L'Aluminium et ses Alliages. C. Grard. 251 pp. Price, 25 fr. Berger-Levrault, Paris.

Chemical Theory: Elementary Chemical Theory and Calculations. Joseph Knox. 2d Ed. 8vo. 109 pp. Gurney & Jackson, London.

Chemistry: Applied Chemistry; A Practical Handbook for Students of Household Science and Public Health. C. K. Tinkler and Helen Masters. Vol. 1. 8vo. Price, 12s. 6d. C. Lockwood & Son, London.

Chemistry: A Course of Practical Chemistry for Agricultural Students. L. F. Newman and H. A. D Neville. Vol 1. 235 pp. Price, 10s. 6d. University Press, Cambridge.

Chemistry: A Foundation Course in Chemistry for Students of Agriculture and Technology. J. W. Dodgson and J. A. Murray. 2d Ed. 8vo. 253 pp. Price, 6s. 6d. Hodder & Stoughton, London.

Coal-tars and Their Derivatives. G. Malatesta. Translated from the First Italian Edition, with Revisions, Corrections and Additions by the Author. 8vo. 530 pp. Price, 21s. E. & F. N. Spon, Ltd., London.

Colloids: The Use of Colloids in Health and Disease. A. B. Searle. 120 pp. Price, 8s. Constable & Co., Ltd., London.

Cosmetics: A Handbook of the Manufacture, Employment, and Testing of All Cosmetic Materials and Cosmetic Specialties with Numerous Recipes. Theodor Koller. Translated from the German. 3d English Edition. 8vo. 264 pp. Price, 8s. 6d. Scott, Greenwood & Son, London.

Foods: The Microbiology and Microanalysis of Foods. Albert Schneider. 8vo. Price, $3.50. P. Blakiston's Son & Co., Philadelphia.

Fuels: Use of Low-Grade and Waste Fuels for Power Generation. J. B C. Kershaw. 202 pp. Price, 17s. Constable & Co., Ltd., London.

Legal Chemistry and Scientific Criminal Investigation. A. Lucas. 8vo. 181 pp. Price, $3.40. Longmans, Green & Co., New York.

Metallography. S. L. Hoyt. Vol. 1. 8vo. 256 pp. Price, $3.00. McGraw-Hill Book Co., New York.

Nitrates, Phosphates, Potash. R. De Bonard. 200 pp. Price, 18 fr. Ch. Béranger, Paris.

Oils, Industrial: Les Huiles Industrielles et leurs Dérivés; Fabrication, Tranformations; Applications. J. Fritsch. 357 pp. Price, 30 fr. A. Legrand, Paris.

Ore Dressing: Handbook of Ore Dressing, Equipment and Practice. A. W. Allen. 12mo. 239 pp. Price, $3.00. McGraw-Hill Book Co., New York.

Organization as Applied to Industrial Problems. H. T. Wright. 21s. C Griffin & Co., Ltd., London.

Paper: Modern Pulp and Paper Making; A Practical Treatise. G. S. Witham. Price, $6.00. The Chemical Catalog Co., Inc., New York.

Phosphorus: Phosphore, Arsenic, Antimoine. Bibliothèque de Chimie de L'Encyclopédie Scientifique. A. Boutaric and A. Raynaud. 420 pp. Price, 9 fr. 50. G. Doin, Paris.

Soap: Manual of Toilet Soap-Making Comprising Toilet Soaps, Medicated Soaps and other Specialties. C. Deite. 2d Revised English Edition. 8vo. 356 pp. Price, 21s. 9d. Scott, Greenwood & Son, London.

Steel: Hardening, Tempering, Annealing and Forging of Steel, Including Heat Treatment of Modern Alloy Steels. J. V. Woodworth. 5th Ed. 8vo. 321 pp. Price, $3.00. N. W. Henley Pub. Co., New York

Volatile Oils. E. Gildemeister. Translated by Edward Kremers 2 Vols. 2d Ed. 8vo. Price, $7.50 each John Wiley & Sons, Inc., New York.

Volumetric Analysis. G. S. V. Wills. 8vo. 96 pp. Price, 5s. Wills and Woodnoth, London.

Water Purification Plants and Their Operation. M. F Stein. 2d Ed Revised. 8vo. 258 pp. Price, $3.00. John Wiley & Sons, Inc , New York.

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Aluminum: Rate of Corrosion of Aluminum. G. H. Bailey. *Journal of the Society of Chemical Industry*, Vol. 39 (1920), No. 9, pp. 118*t*–120*t*.

By-Product and Producer Gas Plant: The Lay-out and Operation of a By-Product Producer Gas Plant. W. H. Patchell. *Engineering and Industrial Management*, Vol. 3 (1920), No. 20, pp. 619–622.

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Cyanide: Canadian Cyanide: Its Manufacture and Utilization. W. S. Landis. *Canadian Chemical Journal*, Vol. 4 (1920), No. 5, pp. 130–132.

Cyanogen Chloride: The Preparation of Cyanogen Chloride on a Large Laboratory Scale. T. S. Price and S. J. Green. *Journal of the Society of Chemical Industry*, Vol. 39 (1920), No. 8, pp. 98*t*–101*t*.

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Dyeing: Para Red Dyeing. A. J. Hall. *Color Trade Journal*, Vol. 6 (1920), No. 6, pp. 177–179.

Dyestuff Industry: National Foreign Policies Important for Development of American Dyestuff Industry. L. W. Alwyn-Schmidt. *Color Trade Journal*, Vol 6 (1920), No. 6, pp. 159–62.

Dyestuffs: Chemical and Physical Properties of Dyestuffs. Acid and Basic Dyes in Gelatin Solutions. J. Traube and F. Koehler. *Scientific American Monthly*, Vol. 1 (1920), No. 5, pp. 408–411.

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Turbine Steels. A Research into Their Mechanical Properties. W. H. Hatfield. *Engineering and Industrial Management*, Vol. 3 (1920), No. 14, pp. 425–426.

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Zinc Industry of the Tri-State (Oklahoma, Missouri and Kansas) Field. F. J. Tietsort. *Compressed Air Magazine*, Vol. 25 (1920), No. 5, pp. 9635–9643.

MARKET REPORT—JUNE, 1920

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

		June 1	June 15
Acid, Boric, cryst., bbls.	lb.	.18	.18
Hydrochloric, com'l, 22°	lb.	.03½	.03½
Hydriodic	oz.	.19	.19
Nitric, 42°	lb.	.08½	.08½
Phosphoric, 50% tech	lb.	.25	.25
Sulfuric, C. P.	lb.	.07	.07
Chamber, 66°	ton	22.00	22.00
Oleum	ton	28.00	28.00
Alum, ammonia, lump	lb.	.04	.04
Aluminum Sulfate (iron-free)	lb.	.04	.04
Ammonium Carbonate, pwd	lb.	.14½	.16
Ammonium Chloride, gran	lb.	.18	.15
Ammonia Water, carboys, 26°	lb.	.10	.10
Arsenic, white	lb.	.14½	.15
Barium Chloride	ton	160.00	175.00
Nitrate	lb.	.12	.11
Barytes, white	ton	30.00	30.00
Bleaching Powd., 35%, Works,	100 lbs.	5.50	5.50
Borax, cryst., bbls.	lb.	.09½	.09½
Bromine, tech., bulk	lb.	.85	.85
Calcium Chloride, fused	ton	27.50	27.50
Chalk, precipitated, light	lb.	.05	.05
China Clay, imported	ton	18.00	18.00
Copper Sulfate	100 lbs.	8.25	8.25
Feldspar	ton	8.00	8.00
Fuller's Earth	100 lbs.	1.25	1.25
Iodine, resublimed	lb.	4.35	4.35
Lead Acetate, white crystals	lb.	.15	.15
Nitrate	lb.	.15	.15
Red American	100 lbs.	.10½	.10½
White American	100 lbs.	.09½	.09½
Lime Acetate	100 lbs.	3.50	3.50
Lithium Carbonate	lb.	1.50	1.50
Magnesium Carbonate, Tech	lb.	.12	.12
Magnesite	ton	65.00	65.00
Mercury flask	75 lbs.	80.00	90.00
Phosphorus, yellow	lb.	.35	.35
Plaster of Paris	100 lbs.	1.50	1.50
Potassium Bichromate	lb.	.45	.44
Bromide, Cryst	lb.	.95	.95
Carbonate, calc., 80–85%	lb.	.18	.18
Chlorate, cryst.	lb.	.15	.15
Cyanide, bulk, 98–99%	lb.	.30	.30
Hydroxide, 88–92%	lb.	.32	.33
Iodide, bulk	lb.	3.35	3.35
Nitrate	lb.	.14	.14
Permanganate, U. S. P.	lb.	.90	.90
Salt Cake	ton	32.00	32.00
Silver Nitrate	oz.	.63	.58
Soapstone, in bags	ton	12.00	12.00
Soda Ash, 58%, bags	100 lbs.	3.65	3.65
Caustic, 76%	100 lbs.	6.50	6.50
Sodium Acetate	lb.	.12	.12
Bicarbonate	100 lbs.	3.00	3.00
Bichromate	lb.	.33	.32
Chlorate	lb.	.10	.10
Cyanide	lb.	.27	.27
Fluoride, technical	lb.	.18	.18
Hyposulfite	100 lbs.	3.60	3.60
Nitrate, 95%	100 lbs.	3.85	3.85
Silicate, 40°	lb.	.02	.02
Sulfide	lb.	.10¼	.10¼
Bisulfite, powdered	lb.	.06½	.06½
Strontium Nitrate	lb.	.27	.27
Sulfur, flowers	100 lbs.	3.75	3.75
Crude	long ton	30.00	30.00
Talc, American, white	ton	20.00	20.00
Tin Bichloride	lb.	.21½	.21½
Oxide	lb.	.60	.60
Zinc Chloride, U. S. P.	lb.	.50	.50
Oxide, bbls.	lb.	.22	.22

ORGANIC CHEMICALS

		June 1	June 15
Acetanilid	lb.	.75	.75
Acid, Acetic, 28 p. c.	100 lbs.	4.00	4.00
Glacial	lb.	.17	.17
Acetylsalicylic	lb.	.95	.95
Benzoic, U. S. P., ex-toluol	lb.	.85	.85
Carbolic, cryst., U. S. P., drs.	lb.	.15	.15
50- to 110-lb. tins	lb.	.21	.23
Acid (*Concluded*)			
Citric, crystals, bbls.	lb.	1.03	.99
Oxalic, cryst., bbls.	lb.	.58	.60
Pyrogallic, resublimed	lb.	2.50	2.50
Salicylic, bulk, U. S. P.	lb.	.55	.55
Tartaric, crystals, U. S. P.	lb.	.84	.82
Trichloracetic, U. S. P.	lb.	4.40	4.40
Acetone, drums	lb.	.22	.22
Alcohol, denatured, 190 proof	gal.	1.13	1.13
Ethyl, 190 proof	gal.	7.00	7.00
Wood, Pure	gal.	3.50	4.40
Amyl Acetate	gal.	4.00	4.00
Camphor, Jap. refined	lb.	1.80	1.65
Carbon Bisulfide	lb.	.08	.08
Tetrachloride	lb.	.14	.14½
Chloroform, U. S. P.	lb.	.40	.40
Creosote, U. S. P.	lb.	.75	.75
Cresol, U. S. P.	lb.	.18	.18
Dextrine, corn	lb.	.06¼	.06¼
Imported Potato	lb.	.14	.14
Ether, U. S. P., conc., 100 lbs	lb.	.21	.24
Formaldehyde	lb.	.58	.53
Glycerol, dynamite, drums	lb.	.26	.26½
Pyridine	gal.	3.00	3.00
Starch, corn	100 lbs.	5.25	5.25
Potato, Jap.	lb.	.06	.06
Rice	lb.	.25	.25
Sago	lb.	.05	.05

OILS, WAXES, ETC.

		June 1	June 15
Beeswax, pure, white	lb.	.65	.65
Black Mineral Oil, 29 gravity	gal.	.22	.22
Castor Oil, No. 3	lb.	.18	.18
Ceresin, yellow	lb.	.16	.16
Corn Oil, crude	lb.	.16	.16
Cottonseed Oil, crude, f. o. b. mill	lb.	.16	.16
Menhaden Oil, crude (southern)	gal.	.80	.75
Neat's-foot Oil, 20°	gal.	2.25	2.25
Paraffin, 128–130 m. p., ref.	lb.	.11½	.11½
Paraffin Oil, high viscosity	gal.	.45	.45
Rosin, "F" Grade, 280 lbs.	bbl.	20.25	19.05
Rosin Oil, first run	gal.	.90	.83
Shellac, T. N.	lb.	1.00	1.15
Spermaceti, cake	lb.	.30	.30
Sperm Oil, bleached winter, 38°	gal.	1.95	1.95
Stearic Acid, double-pressed	lb.	.27½	.25½
Tallow Oil, acidless	gal.	1.60	1.60
Tar Oil, distilled	gal.	.60	.60
Turpentine, spirits of	gal.	2.45	1.89½

METALS

		June 1	June 15
Aluminum, No. 1, ingots	lb.	.32	.32
Antimony, ordinary	100 lbs.	9.00	8.25
Bismuth	lb.	2.52	2.52
Copper, electrolytic	lb.	.19	.19
Lake	lb.	.18¾	.18½
Lead, N. Y.	lb.	.08½	.08½
Nickel, electrolytic	lb.	.45	.45
Platinum, refined, soft	oz.	95.00	80.00
Quicksilver, flask	75 lbs ea.	80.00	90.00
Silver	oz.	1.01	.90
Tin	lb.	.52½	.50
Tungsten Wolframite	per unit	7.00	7.00
Zinc, N. Y.	100 lbs.	8.50	8.50

FERTILIZER MATERIALS

		June 1	June 15
Ammonium Sulfate	100 lbs.	7.00	7.00
Blood, dried, f. o. b. N. Y.	unit	8.00	8.00
Bone, 3 and 50, ground, raw	ton	48.00	48.00
Calcium Cyanamide, unit of Ammonia		4.00	4.00
Fish Scrap, domestic, dried, f. o. b. works	unit	7.25	7.25
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%	ton	6.85	6.85
Tennessee, 78–80%	ton	11.00	11.00
Potassium Muriate, 80%	unit	2.50	2.50
Pyrites, furnace size, imported	unit	.18	.18
Tankage, high-grade, f. o. b. Chicago	unit	7.75	7.75

COAL-TAR CHEMICALS

		June 1	June 15
Crudes			
Benzol, C. P.	gal.	.35	.35
Cresol, U. S. P.	lb.	.18	.18
Naphthalene, flake	lb.	.16	.21
Phenol, drums	lb.	.15	.15
Toluol, 90%	gal.	.36	.36
Xylol, water white	gal.	.40	.40
Intermediates			
Acids:			
Anthranilic	lb.	2.85	2.85
B	lb.	2.25	2.25
Benzoic	lb.	.85	.85
Broenner's	lb.	1.75	1.75
Cleves	lb.	2.00	2.00
Cresylic, 97–99%	gal.	1.20	1.20
F	lb.	3.50	3.50
Gamma	lb.	2.50	2.50
H	lb.	2.25	2.25
Metanilic	lb.	1.70	1.70
Monosulfonic F	lb.	3.50	3.50
Napthionic, crude	lb.	.85	.85
Neville & Winther's	lb.	1.90	1.90
Phthalic	lb.	.60	.60
Picric	lb.	.25	.25
Sulfanilic	lb.	.35	.35
Tobias'	lb.	2.25	2.25
Amido Azo Benzol	lb.	1.15	1.15
Aniline Oil	lb.	.35	.34
For Red	lb.	.65	.65
Aniline Salt	lb.	.42	.42
Anthracene, 80–85%	lb.	.75	.75
Anthraquinone	lb.	4.50	4.50
Benzaldehyde, tech	lb.	.75	.75
U. S. P.	lb.	1.25	1.00
Benzidine Base	lb.	1.40	1.40
Benzidine Sulfate	lb.	1.15	1.15
Diamidophenol	lb.	6.00	6.00
Dianisidine	lb.	9.00	9.00
p-Dichlorbenzol	lb.	.10	.10
Diethylaniline	lb.	1.40	1.40
Dimethylaniline	lb.	1.25	1.25
Dinitrobenzol	lb.	.36	.36
Dinitrotoluol	lb.	.43	.43
Diphenylamine	lb.	.80	.80
G Salt	lb.	.90	.90
Hydroquinone	lb.	2.00	2.00
Metol	lb.	11.50	11.50
Monochlorbenzol	lb.	.16	.18
Monoethylaniline	lb.	2.15	2.15
a-Naphthylamine	lb.	.45	.45
b-Naphthylamine (Sublimed)	lb.	2.25	2.25
b-Naphthol, crude	lb.	.85	.86
m-Nitraniline	lb.	1.00	1.05
p-Nitraniline	lb.	1.65	1.50
Nitrobenzol, crude	lb.	.16	.16
Rectified (Oil Myrbane)	lb.	.18	.18
p-Nitrophenol	lb.	.80	.80
p-Nitrosodimethylaniline	lb.	2.90	2.90
o-Nitrotoluol	lb.	.25	.25
p-Nitrotoluol	lb.	1.50	1.50
m-Phenylenediamine	lb.	1.15	1.15
p-Phenylenediamine	lb.	2.65	2.65
Phthalic Anhydride	lb.	.45	.45
Primuline Base	lb.	3.00	3.00
R Salt	lb.	.90	.90
Resorcin, tech	lb.	4.00	4.00
U. S. P.	lb.	6.00	6.00
Schaeffer Salt	lb.	.75	.75
Sodium Naphthionate	lb.	1.10	1.10
Thiocarbanilid	lb.	.60	.60
Tolidine, Base	lb.	1.75	1.75
Toluidine, mixed	lb.	.44	.44
o-Toluidine	lb.	.35	.35
m-Toluylenediamine	lb.	1.40	1.40
p-Toluidine	lb.	2.00	2.00
Xylidene, crude	lb.	.45	.45

COAL-TAR COLORS

		June 1	June 15
Acid Colors			
Black	lb.	1.15	1.15
Blue	lb.	3.00	3.00
Acid Colors (*Concluded*)			
Fuchsin	lb.	2.50	3.00
Orange III	lb.	1.00	1.00
Red	lb.	1.10	1.30
Violet 10B	lb.	6.50	6.50
Alkali Blue, domestic	lb.	4.75	5.50
Imported	lb.	8.00	8.00
Azo Carmine	lb.	4.00	4.00
Azo Yellow	lb.	2.00	2.00
Erythrosine	lb.	12.00	12.00
Indigotine, conc.	lb.	3.00	3.00
Paste	lb.	1.50	1.50
Naphthol Green	lb.	1.50	1.50
Ponceau	lb.	1.25	1.35
Scarlet 2R	lb.	1.00	1.00
Direct Colors			
Black	lb.	1.00	1.00
Blue 2B	lb.	.70	.70
Brown R	lb.	1.80	1.80
Fast Red	lb.	3.50	3.50
Yellow	lb.	2.00	2.00
Violet, con't	lb.	2.20	2.20
Chrysophenine, domestic	lb.	2.25	2.25
Imported	lb.	3.80	3.80
Congo Red, 4B Type	lb.	.90	.90
Primuline, domestic	lb.	3.00	3.00
Oil Colors			
Black	lb.	.70	.70
Blue	lb.	1.65	1.65
Orange	lb.	1.40	1.40
Red III	lb.	1.65	1.65
Scarlet	lb.	1.75	1.75
Yellow	lb.	1.70	1.70
Nigrosine Oil, soluble	lb.	.90	.90
Sulfur Colors			
Black	lb.	.20	.20
Blue, domestic	lb.	.70	.70
Brown	lb.	.35	.35
Green	lb.	1.00	1.00
Yellow	lb.	.90	.90
Chrome Colors			
Alizarin Blue, bright	lb.	7.75	7.75
Alizarin Red, 20% Paste	lb.	1.10	1.10
Alizarin Yellow G	lb.	1.00	1.00
Chrome Black, domestic	lb.	1.25	1.25
Imported	lb.	2.20	2.20
Chrome Blue	lb.	2.50	2.50
Chrome Green, domestic	lb.	1.50	1.50
Chrome Red	lb.	2.00	2.00
Gallocyanine	lb.	3.25	3.25
Basic Colors			
Auramine, O, domestic	lb.	2.50	2.50
Auramine, OO,	lb.	4.15	4.15
Bismarck Brown Y	lb.	.90	.90
Bismarck Brown R	lb.	1.20	1.20
Chrysoidine R	lb.	.75	.75
Chrysoidine Y	lb.	.75	.75
Green Crystals, Brilliant	lb.	6.00	6.00
Indigo, 20 p. c. paste	lb.	.85	.85
Fuchsine Crystals, domestic	lb.	5.00	5.50
Imported	lb.	12.00	12.00
Magenta Acid, domestic	lb.	4.25	4.25
Malachite Green, crystals	lb.	4.50	4.50
Methylene Blue, tech	lb	2.50	2.75
Methyl Violet 3 B	lb.	3.00	3.50
Nigrosine, spts. sol	lb.	.85	.85
Water sol., blue	lb.	.65	.65
Jet	lb	.90	.90
Phosphine G., domestic	lb.	7.00	7.00
Rhodamine B, extra conc'd	lb.	35.00	40.00
Victoria Blue, base, domestic	lb.	6.00	6.00
Victoria Green	lb	6.00	6.00
Victoria Red	lb.	7.00	7.00
Victoria Yellow	lb.	7.00	7.00

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CONTENTS

EDITORIALS:

The Chicago Meeting 730
To Your Post 730
Prophetic 731
Professor Bogert Declines 731
How Best to Serve 731
Notes 732

ORIGINAL PAPERS:

A Synthesis of Thymol from *p*-Cymene. Max Phillips and H. D. Gibbs 733
Gasoline from Natural Gas. II—Use of Charcoal in Determining the Gasoline Content of Natural Gas. R. P. Anderson and C. E. Hinckley 735
The Extraction of Bitumens from Mineral Aggregate. M. R. Walczak and H. I. Rice 738
The Action of Ultraviolet Light on the Yeast-like Fungi—I. Bertram Feuer and F. W. Tanner 740
Some Anomalies in the Solidification Point of Tristearin. Ben H. Nicolet 741
Cellulose Phthalate: Its Preparation and Properties. Harold A. Levey 743
The Relative Importance of Some Coloring Matters in Cane Juices and Sirups. F. W. Zerban 744
The Preservation of Eggs, Including a Bibliography of the Subject. Hilton Ira Jones and Robert DuBois. 751
A Volumetric Method for the Detection and Estimation of Neutralizers in Butter and in Certain Allied Products. L. W. Ferris 757
The Heat of Hydration and Specific Heat of Wheat Flour. Farrington Daniels, B. H. Kepner and P. P. Murdick 760
The Kreis Reaction of Cottonseed-Oil Products. W. B. Smith 764
Modification of the Howard Method for Counting Yeasts, Spores, and Bacteria in Tomato Products. Harry M. Miller 766
The Behavior of Phenolphthalein with Iodine and a Method for the Determination of Phenolphthalein. Samuel Palkin 766
The Colorimetric Estimation of Adrenalin. Wilbur L. Scoville 769
A New Method for the Determination of Phenol in the Presence of Certain Other Phenols. Robert M. Chapin 771
The Electrometric Analysis of Arsenicals. Charles S. Robinson and O. B. Winter 775
Rapid Examination of Shellac, Shellac Varnish and Lacquer. T. Linsey Crossley 778
The Freezing Points of Mixtures of Sulfuric and Nitric Acids. Walter C. Holmes 781
Hygroscopicity of By-product Coke. W. A. Selvig and B. B. Kaplan 783
The Determination of Sulfate in Sulfonated Oils. Erwin J. Kern 785

LABORATORY AND PLANT:

Potash from Kelp. III—The Preliminary Examination of Kelp Distillates. G. C. Spencer 786
The Testing of Saccharimeters by Means of the Telescopic Control Tube. C. A. Browne 792
Some Improvements on the Needle Type Thermocouple for Low Temperature Work. George F. Taylor 797
Preparation of Ammonia-Free Water. Gerald C. Baker 798
Notes on the Preparation of Cupferron. D. R. Kasanof. 799
Note on the Use of Alundum Filtering Crucibles. D. T. Englis 799
Rapid Determination of Small Amounts of Copper by the Iodide Method. H. F. Bailey 800
Some American-Made Chemical Reagents. W. D. Collins 800

ADDRESSES AND CONTRIBUTED ARTICLES:

Certain Aspects of the Chemistry of Cellulose Acetate from the Colloidal Viewpoint. Gustavus J. Esselen, Jr. 801
Chemical Control in the Beet Sugar Industry. S. J. Osborn 803
Dye Research. Robert E. Rose 805
Chlorine as a Preventive of Influenza. Harrison Hale. 806
CHEMICAL READING COURSES 806

SCIENTIFIC SOCIETIES:

Canada Meeting of the American Institute of Chemical Engineers; Improvement of Conditions for College Instructing Staffs; Sixth National Exposition of Chemical Industries; Manufacturing Chemists' Association; Cellulose Symposium for the Chicago Meeting of the American Chemical Society; Technical Association of the Pulp and Paper Industry; Calendar of Meetings 812

NOTES AND CORRESPONDENCE:

Uncovering the Platinum Theft at the Old Hickory Powder Plant, Jacksonville, Tennessee; Drawings of Standard Apparatus; Joseph A. Holmes Safety Association; MacMichael Torsional Viscosimeter; The Effect of Air in Steam on the Coefficient of Heat Transmission—Correction 815
WASHINGTON LETTER 818
LONDON LETTER 819
PARIS LETTER 820
INDUSTRIAL NOTES 821
PERSONAL NOTES 822
GOVERNMENT PUBLICATIONS 823
BOOK REVIEWS 827
NEW PUBLICATIONS 830
MARKET REPORT 831

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EDITORIALS

THE CHICAGO MEETING

The Sixtieth General Meeting of the AMERICAN CHEMICAL SOCIETY will be held in Chicago, September 6 to 10, 1920. It is to be designated "Reconstruction Meeting," a thoroughly fitting and timely title, in view of the problems now confronting the nation, especially the all-important question of increased production, whose chief handmaiden chemistry is. It is evident from the activities of the various committees of the Chicago Local Section that preparations are being made for one of the largest gatherings in the history of the SOCIETY, and when this gathering does assemble Chicago chemists will see to it that every available means is placed at its disposal for comfort and entertainment.

Headquarters will be located at the Congress Hotel. Dr. S. L. Redman, in charge of hotel accommodations, writes "it is advisable that members expecting to attend the convention be warned to make their reservations early. These reservations may be made individually by corresponding with any of the hotels listed on the preliminary program. Reservations may also be secured through the Hotel Information Bureau of the Chicago Association of Commerce, which has assumed the responsibility of guaranteeing a comfortable room for every delegate. The management of the Congress Hotel will attempt to secure reservations in other hotels for those who wish to leave the matter in their hands."

On Monday, September 6, the Council will be tendered a luncheon by the Chicago Chemists' Club. Following the afternoon session the Council will be entertained at dinner by the Chicago Section.

The opening meeting of the SOCIETY will be held Tuesday morning at the Congress Hotel. In the afternoon the meeting will be held in Patten gymnasium, Northwestern University. Following the scientific meeting the entertainment committee has provided a unique and delightful program on the university campus. As a substitute for the conventional smoker, the program will include pleasures for both the men and the ladies who are expected in large numbers, a band concert, an organ recital, outdoor sports including a baseball game by the chemists, and enjoyment of the beautiful beach of Lake Michigan. Refreshments will be served on the lawn, and in the evening there will be an entertainment in Patten gymnasium, the details of which are at present veiled in mystery.

Divisional meetings begin on Wednesday morning and will be held in the lecture rooms of the University of [illegible]. Thorough arrangements are under way for the convenient posting of the progress of the program in each division, so that papers before different divisions can be attended as desired.

Wednesday evening Dr. W. A. Noyes will deliver the presidential address, and on Thursday evening the annual dinner will be held. A series of excursions to many interesting industrial plants is being arranged.

All in all a very profitable and delightful week is in prospect for those who have the good fortune to attend this important meeting of the SOCIETY. The successful carrying out of the extensive program is assured by the fact that it is in the hands of the Chicago Section, whose membership has been drawn upon for thoroughly live, energetic committees. The chairmen of the several committees are:

Honorary Chairman: JULIUS STIEGLITZ; *Finance:* W. A CONVERSE; *Publicity:* CHESTER H. JONES; *Excursions:* H. MCCORMACK; *Registration and Information:* G. H. PICKARD; *Hotels:* S. L. REDMAN; *Transportation:* A. E. SCHAAR; *Program:* J. A. HYNES; *Banquet:* D. K. FRENCH; *Men's Entertainment:* HERBERT N. MCCOY; *Ladies' Entertainment:* ETHEL M. TERRY; *Relation to Other Scientific Societies:* WM. HOSKINS.

The officers of the Chicago Section are:

Chairman: W. LEE LEWIS; *Convention Secretary:* R. J. QUINN; *Convention Treasurer:* F. M. DEBEERS.

TO YOUR POST!

The action of Congress in making the Chemical Warfare Service an independent unit in the War Department has aroused the active enthusiasm of the former members of the Service whose remarkable achievements during the war won such high commendation from all quarters. This enthusiasm led some seventy members of the Chemical Warfare Service Post of the American Legion to gather for dinner around the tables of "Billy the Oysterman," in New York City, on Wednesday evening, July 14, 1920.

The purpose of the gathering was the revival of the Post. The guest of honor was Col. Amos A. Fries, who made a stirring address upon the present work of the Service, its importance in future wars, and the need of the closest possible coöperation with civilian chemists, especially with those who had served it so loyally in the past.

The gathering felt that the meeting should be considered merely as preliminary to a larger and more representative meeting which it is proposed to hold during Exposition Week, September 20 to 25, 1920. The following temporary officers were elected:

President: LESLIE T. SUTHERLAND
Vice President: G. A. BURRELL
Vice President: WILLIAM NOONAN
Secretary: R. P. ROSE
Treasurer: F. G. ZINSSER
Executive Committee: G. A. BURRELL, W. H. WALKER, BRADLEY DEWEY, F. M. DORSEY, W. S. BACON, MAYO SMITH
Personal Assistant to the President in the Work of Reorganization: E. M DUNN

By unanimous vote the Post adopted a resolution opposing a bonus for able-bodied veterans of the world war, but urged that all possible provisions be made for wounded men.

The revival of the Chemical Warfare Service Post is a step which should appeal to all former members of the Service. No eye of a prophet is needed to foretell the size and the enthusiasm of the September gathering. There is work to be done, important work, and without doubt that work can be done best through such an organization, ready at call for whatever may need to be done. The Service is an integral part of the Army. Its future usefulness cannot be overestimated. Let the Service back the Army and the Army back the Service.

. . . .

On July 16, 1920, Colonel Fries was appointed Chief of the Chemical Warfare Service by President Wilson. As the Act of Congress for the reorganization of the Army specifies that the head of this Service shall rank as Brigadier General, this appointment therefore restores to General Fries the title which he so worthily won at the Front.

The appointment will bring deepest satisfaction to all civilian chemists and will enlist their enthusiastic support of that branch of the Army which is capable of such great development.

PROPHETIC

The continued illness of the Commissioner of Internal Revenue has prevented his consideration of the views presented at the hearing on June 16, 1920, regarding industrial and tax-free alcohol. It is felt that the Commissioner will take a thoroughly sympathetic attitude toward the proposals made at the hearing looking to stimulation of production and facilitation of distribution of this all-important chemical reagent, for the wording of the National Prohibition Act is so clear that the intent of Congress cannot be misunderstood.

Support of some of the statements made at the hearing is furnished by the words of a former Commissioner of Internal Revenue, Hon. John G. Capers. In the "Denatured Alcohol Number" of *Harper's Weekly* of October 3, 1908, Mr. Capers wrote:

> We cannot hope to attain the full development or success in the production of denatured alcohol which is peculiar to Germany—and for several reasons. In the first place, denatured alcohol is a matter of nearly as much concern to the Empire as its army or navy. In fact, the elder Emperor inaugurated the industry for the primary purpose of having a source of light, heat, and power within the German Empire independent of the petroleum products, of which Germany has none. *The wise old Emperor, realizing that some day his Empire might be forced, in time of war, to be self-dependent and resourceful within its own borders, determined to be independent of petroleum products, all of which were and still are shipped into Germany from other countries,* and an elaborate paternal system was inaugurated to insure, as the government's alternate safety source of light, heat, and power, the alcohol which could be produced from the German potato, now so carefully cultivated for that purpose, as it has been for nearly forty years. The large German farmer must account for every gallon, must turn back into the land he cultivates all waste material and useless by-products from his distillery. In fact, a paternalism, a governmental guardianship over the production of alcohol exists as a fixed policy of Germany which would not and could not be maintained under our form of government here in the United States.

Uncannily prophetic and extremely interesting historically!

PROFESSOR BOGERT DECLINES

Professor M. T. Bogert, recently nominated a Tariff Commissioner by President Wilson, has reluctantly declined the appointment. While recognizing the need of a chemist on the Commission, Professor Bogert felt compelled to decline the appointment because of the brevity of the term, the uncertainty of Senate confirmation, and doubt as to the supporting hand of Congress in voting appropriations of sufficient magnitude to enable the Commission to discharge promptly and efficiently the multitudinous and highly important responsibilities devolving upon it.

We hope Professor Bogert is wrong as to the attitude of Congress, for the value of the service already performed by the Commission commends itself to many men of all parties. We can readily understand his unwillingness to give up the important position which he holds on the staff of Columbia University, a position not affected by political whims, carrying a good salary and an assured pension on retirement, not to mention the happiness of the experienced teacher in the association with a large group of advanced students through whose training he can hope to increase multifold his usefulness to the country.

HOW BEST TO SERVE

Chemical and Metallurgical Engineering (June 23, 1920, page 1142) is disturbed because "chemists were not more largely represented on the floor" of the organizing conference of the Federated American Engineering Societies, and because the AMERICAN CHEMICAL SOCIETY did not send "deputies" to the meeting. Some one, whether a chemist or a federate is not stated, dismissed the matter briefly "by the statement that chemists are not engineers." Then our good neighbor becomes stern and exclaims—"Holding the opinion that the Chemical Society should have been represented, it is not so easy to excuse absence in that manner," and thereupon risks "the chance of tedium" by advancing "a few thoughts" on the relationships of engineers.

We have read the "thoughts" carefully, but we confess we are muddled. By laborious argument Dr. Stieglitz was proved to be "in no sense an engineer; he is a scientist. Dr. Little, on the other hand, is an engineer primarily" and, inferentially, we suppose not a scientist. Further "it seems most fit that engineers . . . distinguished from scientists . . . should organize . . ." Surely no member of the AMERICAN CHEMICAL SOCIETY would argue to the contrary.

It seems that the American Institute of Chemical Engineers was duly represented. Certainly that was most eminently fitting and to be expected. They are all engineers, they must be in order to be eligible for membership in the Institute.

Time and again this matter of joining with the engineers in some such movement has been brought to the consideration of the officers of the AMERICAN CHEMICAL SOCIETY. The matter has been discussed from every angle, and on each occasion it has been the unanimous opinion that it would be unwise for the SOCIETY to participate. The specific problems of the engineer and the chemist are too far apart to warrant such a union. Wherever problems a mutual the chemist has already practically s those which the engineer is now just be take up. In solving these the chemist has operated on a very compact, efficient, and inexpensive machine. Now he is upbraided for not becoming a part of an enormous, untried, and expensive machine. According to the constitution adopted in Washington on June 4 the AMERICAN CHEMICAL SOCIETY would be assessed $1.50 per member, amounting at present to more than $24,000. Would each of the members of the SOCIETY be willing to assess himself $1.50 in addition to his regular dues, for the purpose of again doing those things which he has already largely done for himself, and to lose his freedom of action by merging himself into a larger group which is to experiment with a bulky machine which we hope will work effectively, but whose success is yet to be demonstrated?

In the concluding paragraph of the editorial the reproof is voiced: "If the AMERICAN CHEMICAL SOCIETY desires to function in public affairs—and we know it has been urging individual chemists to do so—then why has it not embraced this opportunity to join in the creation of a body for that very purpose?" The SOCIETY does function, and functions effectively, in public affairs wherever chemistry is involved, but it feels that this can be done best through its own national organization. It never hesitates to express itself by formal resolution on matters where it feels the country has a right to look to it for expert opinion, its official representatives constantly appear before congressional committees, its members act officially in an advisory capacity to government bureaus, it promptly tendered to the Government its complete, classified census of chemists at the very outbreak of the war, it aids the daily press through a News Service which furnishes weekly bulletins on chemical subjects popularly presented, and in 1916 it coöperated with the four great engineering societies in the all-important work of mobilization of our industrial resources in anticipation of the probability that our country would be drawn into the war.

This last-named "public function" is the most convincing proof that whenever "the interests of the public" involving the coöperation of chemist and engineer are really concerned, there can never be any question of the wholehearted and effective character of that coöperation. Meanwhile, there are still important matters ahead for the AMERICAN CHEMICAL SOCIETY as a distinct entity, and while trying to meet these obligations it holds nothing but the best of good wishes for the success of the Federated American Engineering Societies, whose name, like that of the AMERICAN CHEMICAL SOCIETY, defines exactly what it is.

NOTES

Congratulations to Dr. E. F. Ladd, president of the North Dakota Agricultural College, and for many years professor of chemistry in the same institution, who has just been nominated United States Senator. Dr. Ladd's lifelong fight against the adulteration of food and paint gives assurance that, if elected, he will line up squarely in favor of legislation against any form of sham or fraud. The chemist as a type is steadily emerging. The West by birthright has the pioneering habit.

The officers of the National Exposition of Chemical Industries have taken up vigorously the suggestion in the editorial entitled "Rope Making" in our July issue. Correspondence is in active progress with the Canadian chemists, who are to be the hosts of the Society of Chemical Industry when it visits America in 1921. All of the American past-presidents of the British organization, Drs. Chandler, Remsen, Nichols, and Bogert, and President Noyes of the American Chemical Society, are joining in the effort to bring about a great gathering of British, Canadian, and American chemists in September 1921.

The Library Committee of the Chemists' Club is asking manufacturers and others engaged in the chemical and allied industries to subscribe $100 each to complete the Club library and to sustain a proper service. A wide response to this very moderate request can be safely predicted. The large and numerous investments in industrial research laboratories cannot be fully realized upon until we have in this country at least one great reference library. There is nothing adequate at the present time. The task of upbuilding is too great for any one concern; it becomes easy when all participate. Each hundred so invested will save thousands of dollars as the years go by.

The election of Sir William J. Pope to the presidency of the Society of Chemical Industry will be hailed as an event of unusual significance. That this talented professor in Cambridge University has been selected as leader for the coming year by the industrial chemists of Great Britain is indicative of a close bond between university and industrial chemists. It is already evident that the fundamental policy of the new president will be the greater centralization and unification of all of the chemical interests of Great Britain. Success to him in his progressive efforts!

M. Charles Lormand, a member of the Executive Committee of *Chimie et Industrie*, will furnish a monthly letter from Paris to THIS JOURNAL beginning with this issue. M. Lormand is well known to many American chemists, having served for eight months in Washington and New York as liaison officer with our Chemical Warfare Service. Continuous growth in chemistry is a matter not only of national concern but also of highest portent to those three great nations whose chemists were suddenly called upon to exert their skill to the utmost in unexpected lines during the recent war. Coöperation was effective during those days of stress; for its continuation mutual knowledge of developments in each country is essential.

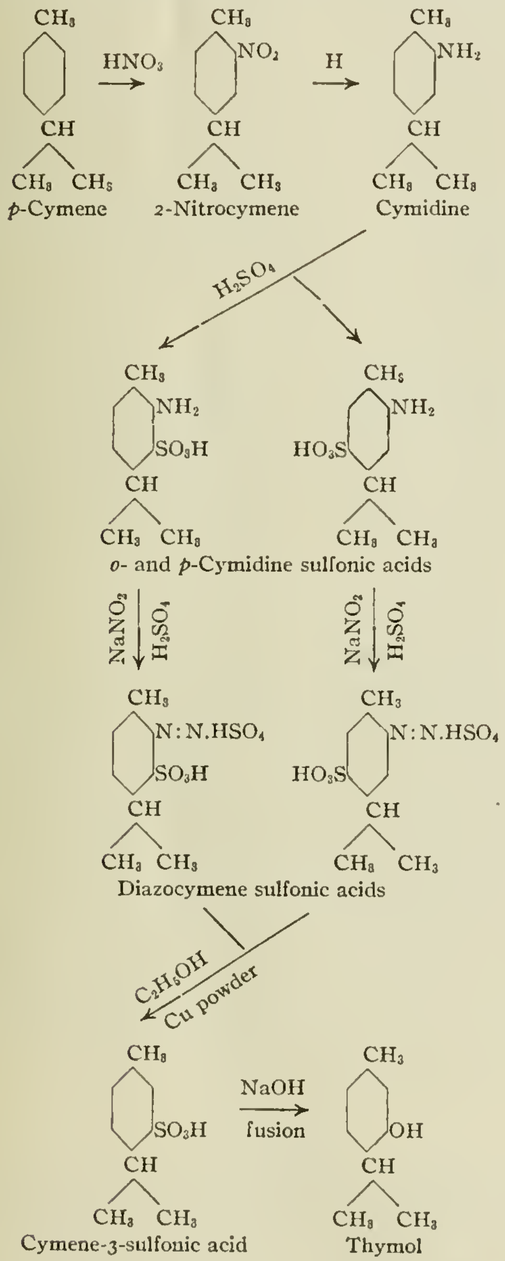
ORIGINAL PAPERS

A SYNTHESIS OF THYMOL FROM *p*-CYMENE

By Max Phillips and H. D. Gibbs
Color Laboratory, Bureau of Chemistry, Washington, D. C.

Received April 7, 1920

When *p*-cymene, 1-methyl-4-isopropyl benzene, is sulfonated or nitrated, substitution takes place very largely in the position ortho to the methyl group.



Although it has been reported that the second isomer also forms during the sulfonation or nitration, its relative amount is too small to be of any practical value. Hence the two common methods of making phenols from their corresponding hydrocarbons, *viz.*, (1) decomposition of the diazo derivative, especially the sulfate, with boiling water and (2) fusion of the sulfonic acid with potassium or sodium hydroxide, cannot be used in making thymol from *p*-cymene. In order to bring about this synthesis an indirect method must be adopted, and of the several possible methods the one outlined herewith was used.[1]

As indicated above, both the *o*- and *p*-cymidine sulfonic acids may be formed by sulfonating cymidine. However, so far as the synthesis of thymol is concerned, it is immaterial which is formed, since both give one and the same cymene sulfonic acid.

HISTORICAL REVIEW

Thymol was first synthesized by Widman[2] in 1882. This classical synthesis very well illustrates the rather indirect method that has to be used. Starting with cuminal, nitro-cuminal was prepared, the nitro group entering the position meta to the aldehyde group. This compound when treated with phosphorus pentachloride was converted into nitro-cymyline chloride, which on reduction with zinc and hydrochloric acid gave 3-aminocymene, and upon diazotization and subsequent hydrolysis thymol resulted.

Thymol has since been synthesized by a number of chemists,[3] but only two of these syntheses need be considered in this connection because of their close relationship to the present method.

Dinesmann[4] obtained a patent on a process of making thymol from 2-brom-*p*-cymene. This process consists in sulfonating 2-brom-*p*-cymene, obtaining 2-brom-3- or 5-sulfonic acid, which when heated with zinc dust and ammonia in an autoclave at 170° gives cymene 3-sulfonic acid. This compound on fusion with potassium hydroxide gives thymol.

Recently a patent has been granted to Andrews[5] on a process of making thymol from cymidine (2-aminocymene). Cymidine is first acetylated, then nitrated, whereupon the nitro group enters meta to the methyl group. The acetyl group is hydrolyzed off and the amino group removed through diazotization and subsequent reduction of the diazo compound with alkaline stannous chloride or with boiling alcohol. The nitro compound thus obtained is then reduced to the corresponding amino compound, which on diazotization and subsequent hydrolysis gives thymol.

EXPERIMENTAL

ISOLATION OF *p*-CYMENE FROM CRUDE OIL—The starting material for this work was *p*-cymene isolated from a crude oil obtained from a sulfite spruce pulp mill. The oil after standing over lime for about a week was subjected to steam distillation. To the distillate about one-fourth its volume of sulfuric acid was added, and the mixture stirred in the cold by means of a mechanical stirrer. After 2 hrs. stirring the dark acid was separated from the oil, a fresh quantity of sulfuric acid added and the stirring continued. This operation was carried on until a sample of the oil after being washed with water gave a very slight yellowish color when shaken with sulfuric acid. The oil was then washed with water, dried over calcium chloride, and distilled over sodium, using a Glinsky still head. Practically all of the material came over from 174° to 175° (759.6 mm. pressure), leaving only a small amount of dark-colored oil in the flask.

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[1] Phillips, U. S. Patent 1,332,680 (1920).

[2] *Ber.*, **15** (1882), 166.

[3] *Ibid.*, **29** (1896), 420; *Nachr. kgl. Ges. Göttingen*, 1903, 223; *Ber.*, **39** (1906), 1163; **41** (1908), 3993.

[4] D. R. P., 125,097 (1900).

[5] U. S. Patent 1,306,512 (1919).

PREPARATION OF NITROCYMENE AND CYMIDINE—For the preparation of nitrocymene the method developed in this laboratory[1] was used. The nitro group enters in the ortho position with respect to the methyl group. The reduction of this compound to aminocymene or cymidine was accomplished by means of iron powder and hydrochloric acid in exactly the same way as nitrobenzene is reduced to aniline.

CONVERSION OF CYMIDINE TO CYMIDINE SULFONIC ACID—Cymidine sulfonic acid was first prepared by Widman[2] in 1886. Starting with cymidine sulfate, he prepared the sulfonic acid by heating one part of the sulfate with two parts of fuming sulfuric acid at 160° to 165° until a test portion, when made alkaline with sodium hydroxide solution, showed the complete absence of globules of cymidine. Using his method, only small quantities of the sulfonic acid could be obtained, the yield being in the neighborhood of 4 to 5 per cent of the theory. A considerable amount of material decomposed during the process of heating with the fuming acid. The method adopted was essentially the same as that used in the preparation of sulfanilic acid by the so-called "baking process."[3] The process was carried out as follows: To 61 cc. of concentrated sulfuric acid 160 g. of cymidine were added in small quantities at a time, stirring after each addition of the cymidine. The cymidine sulfate was placed in an oven and heated for 6 hrs. at about 200°. The mass on cooling was ground and dissolved in hot water. Upon making the solution distinctly alkaline with sodium hydroxide the cymidine which had escaped sulfonation separated as an oil and was recovered by steam distillation. The residue in the flask was concentrated, if necessary, boiled with animal charcoal, filtered, and acidified with hydrochloric acid. Cymidine sulfonic acid separated out as a crystalline mass. The yield of cymidine sulfonic acid was about 30 g. (32 per cent yield calculated on the 60 g. of cymidine actually used up) and the unused cymidine recovered amounted to 100 g. An analysis of the cymidine sulfonic acid for sulfur gave the following results:

Per cent S Found	Per cent S Calculated for $C_{10}H_{12}.NH_2.SO_3H$
14.12	13.98
14.16	...

DIAZOTIZATION OF CYMIDINE SULFONIC ACID AND ITS CONVERSION INTO CYMENE 3-SULFONIC ACID—Widman[4] in 1886 prepared diazocymene sulfonic acid by suspending cymidine sulfonic acid in dilute alcohol and diazotizing in the cold with nitrous acid. However, his attempt to convert this compound into cymene 3-sulfonic acid was not successful, as an ethoxy derivative of it was obtained. That the diazo group of certain compounds, when boiled with alcohol, is replaced by the ethoxy group instead of hydrogen, has been observed by a number of chemists.[1] It has been found, however, that when certain substances such as copper powder, zinc dust, sodium ethylate, sodium hydroxide, potassium carbonate, or sodium methylate are added to the diazo compound, complete reduction takes place without the formation of the ethoxy derivative.[2] For the preparation of cymene 3-sulfonic acid from cymidine sulfonic acid, the following modification of Widman's method was used: One-tenth of a mole (22.9 g.) of the cymidine sulfonic acid was suspended in about 400 cc. of 95 per cent alcohol, 20 cc. concentrated sulfuric acid added, and diazotized in the cold in the usual manner. After diazotization the solution was allowed to stand in the cold for an hour, and then 10 g. of copper powder were added in small quantities at a time, allowing the rapid evolution of nitrogen to subside before making any further additions. The mixture was filtered and the filtrate distilled on the water bath. The residue in the flask was diluted with water, boiled with barium carbonate, filtered, and the filtrate containing the barium salt of cymene 3-sulfonic acid was treated with sodium carbonate and the sodium salt of the sulfonic acid obtained. This sodium salt was converted into thymol, as follows: Thirty grams of 98 per cent sodium hydroxide were treated with a little water and heated in a nickel crucible, with stirring, to 280°. To this 10 g. of the sulfonate were added, with stirring. After all the salt had been added the temperature was raised to 310° and kept there for about 15 min., when the reaction was complete. The melt on cooling was dissolved in water, acidified with hydrochloric acid, and steam distilled. The distillate was extracted with ether, dried over anhydrous sodium sulfate and fractionated after distilling off the ether. Nearly all of the product distilled over at the boiling temperature of thymol. From one-tenth of a mole of cymidine sulfonic acid about 6 g. of thymol oil could be obtained (a 40 per cent yield calculated on the cymidine sulfonic acid used). The thymol obtained was identified by its phenylurethane derivative (m. p. 107°).

SUMMARY

Thymol has been synthesized from *p*-cymene. The process consists in nitrating *p*-cymene; reducing this 2-nitrocymene to 2-aminocymene or cymidine; sulfonating the cymidine by the "baking process" used in the preparation of sulfanilic acid; diazotizing the cymidine sulfonic acid; reducing this to cymene 3-sulfonic acid, and finally fusing the sodium salt of this acid with sodium hydroxide.

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[1] This Journal, **10** (1918), 453.

[2] *Ber.*, **19** (1886), 246.

[3] *Z. angew. Chem.*, **9** (1896), 685

[4] *Loc. cit.*

[1] *Ann.*, **172** (1874), 215; **198** (1879), 25; *Ber.*, **17** (1884), 1887; **17** (1884), 1917; **17** (1884), 2703; *Ann.*, **230** (1884), 286; *Ber.*, **18** (1885), 65.

[2] *Am. Chem. J.*, **16** (1894), 235; **19** (1897), 163; **20** (1898), 298.

GASOLINE FROM NATURAL GAS. II—USE OF CHARCOAL IN DETERMINING THE GASOLINE CONTENT OF NATURAL GAS

By R. P. Anderson and C. E. Hinckley

United Natural Gas Company, Oil City, Pennsylvania

Received December 31, 1919

The first paper of this series was devoted to a discussion of the methods that may be employed for the commercial extraction of gasoline from natural gas. For the purpose of determining whether a gasoline plant shall be installed on gas from a given source and in determining what the nature of the plant shall be, a knowledge of the gasoline content of the gas is of prime importance. Methods of determining the approximate gasoline content of natural gas, embodying the same principles as are used in the production of gasoline commercially, have been employed by the various companies engaged in this industry. All of these methods have undesirable features, and the need for a new method by which tests can be made more quickly and more simply has been strongly felt.

With the recent production of large amounts of gas-mask charcoal, far superior as an adsorbent to any hitherto prepared, came the utilization of this material for determining the gasoline content of natural gas, and results of some of the experimental work on this new method have already been published.[1] In the present paper the authors present the results that they have obtained in standardizing the procedure for the use of charcoal in gas testing and in developing a portable testing outfit.

METHOD OF GASOLINE ADSORPTION

In the experiments to be described 8 to 14 mesh charcoal obtained from the National Carbon Company and known by them as activated carbon, No. 4 mix, was employed in glass tubes about 0.8 in. in diameter. Each tube was filled to a depth of about 8 in. and the removal of the gasoline-forming constituents from the gas was effected by passing it through two of these tubes in series. The weight of the charcoal in each tube amounted to about one ounce. Among the variables which might influence the yield of gasoline the following have been studied: (*a*) Rate of flow of gas through charcoal, (*b*) quantity of gas treated, (*c*) moisture content of gas and charcoal, and (*d*) temperature of gas and charcoal.

(*a*) RATE OF FLOW OF GAS—In varying the rate of flow of gas through the charcoal it was found that, on a gas yielding 0.15 gal. gasoline per M cu. ft., rates from 20 to 50 cu. ft. per hr. gave about the same results.[2] Inasmuch as the amount of gas required for a test is small, the effect upon the yield of gasoline of employing higher rates was not determined.

During the passage of natural gas through charcoal, adsorption of each of its constituents presumably takes place to a certain extent. It is possible to conceive of a variation in the ratio of the adsorbed gasoline-forming constituents to the other adsorbed substances, as a result of a variation in the rate of flow of the gas. Since the efficiency of recovery in liquid form of the gasoline hydrocarbons adsorbed by the charcoal is a function of the amount of gas liberated from the charcoal during the distillation process, the variation in the ratio mentioned above would affect the yield of gasoline at rates which would give complete removal of the gasoline-forming constituents from the gas. While this factor might prove important under certain conditions, it is evident that it has but little effect between rates of 20 and 50 cu. ft. per hr. for the gas which was employed.

For the relationship between rate of flow and charcoal temperature, see (*d*).

(*b*) QUANTITY OF GAS TREATED—The quantity of gas to be employed to obtain the maximum yield of gasoline can be determined only by experiment. If too small an amount of gas is used the ratio of adsorbed gasoline-forming constituents to other adsorbed substances is low and, on distilling the gasoline vapor from the charcoal, the efficiency of recovery of the gasoline is also low, on account of the low partial pressure of the gasoline hydrocarbons in the gas liberated from the charcoal. On the other hand, if too much gas is passed through the charcoal, the gasoline-forming constituents are not completely adsorbed, and a low yield may therefore result. It is quite possible, in the case of certain natural gases, that the efficiency of gasoline recovery in the distillation process might increase more rapidly than the efficiency of adsorption would decrease as the amount of gas first exceeds the limit for complete removal of the gasoline hydrocarbons, and, under these conditions, a maximum yield will be obtained when the volume of gas is in excess of that from which the charcoal can remove the gasoline hydrocarbons with 100 per cent efficiency.

For the amount of charcoal that has been specified, the volume of gas that should be employed may vary with the character of the gas from a fraction of 1 cu. ft. to 30 cu. ft. or more. As regards the gases that the authors have examined, the volume of gasoline recovered from the first charcoal tube should be between 5 and 10 cc., while the volume obtained from the second tube should not exceed a few tenths of 1 cc. A larger volume in the second tube indicates the use of too large a quantity of gas.

The importance of using the proper volume of gas is shown by the data of Table I obtained on a lean gas of about 0.65 specific gravity.

TABLE I

Volume of Gas Cu. Ft.	Volume Gasoline Recovered, Cc. First Tube	Second Tube	Total	Yield Gasoline Gal. per M Cu Ft.
2.7	0.3	...	0.3	0.029
5.5	1.1	Trace	1.1	0.053
10.9	3.3	0.1	3.4	0.082
16.4	7.0	0.2	7.2	0.116
21.8	9.0	0.3	9.3	0.113

In view of the rather narrow limits within which the gas volume must sometimes be chosen, it is important, in examining a natural gas for gasoline for the first time, to make at least three different determinations with different volumes of gas, using whatever information may be available in deciding what volumes to employ.

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[1] Oberfell, Shinkle and Meserve, THIS JOURNAL, **11** (1919), 197; Oberfell and Burrell, *Gas Record*, [2] **16** (1919), 45.

[2] In these and subsequent experiments where the effect of a certain variable was being studied, the experiments were performed in pairs, the conditions being the same except for a single variable. In this way the effect of unavoidable variations in the quality of the gas was eliminated.

(*c*) MOISTURE CONTENT OF GAS AND CHARCOAL—Experiments were performed to determine the effect upon the yield of gasoline of drying the gas before passing it through the charcoal, in some cases using charcoal in equilibrium with the air of the laboratory as regards moisture content, and in others using charcoal that had been dried at 150° C. Drying the gas alone gave an increase in yield of about 5 per cent as the average of three experiments, and drying both gas and charcoal gave an increase in yield of about 8 per cent as the average of the same number of determinations. Inasmuch as the gas volumes employed were probably slightly in excess of the volumes that would give a maximum yield, it seems likely that the effect of drying the gas and charcoal could be made still smaller by using the proper gas volumes. At any rate, the increase in yield as a result of drying the gas and charcoal seems scarcely worth the extra effort, and in subsequent determinations no attempt has been made to modify the natural water content of either the gas or charcoal.

(*d*) TEMPERATURE OF GAS AND CHARCOAL—While it is realized that the activity of charcoal is affected by its temperature, it is felt that such changes in atmospheric temperature as are met with in the ordinary conditions of testing would have but little effect upon the yield of gasoline. On the other hand, when natural gas is first passed through charcoal considerable heat is evolved and when the flow of gas is rapid the temperature of the charcoal may momentarily be raised to a temperature of 50° or 60° C. or even higher in the case of gases rich in easily adsorbable constituents. If a thorough study of the effect of the rate of flow of gas upon the yield of gasoline were to be made with the idea of increasing the accuracy of the charcoal method, the heat of adsorption would probably prove an important factor, especially with gases of large gasoline content.

One experiment has been performed in which gas from the same source was passed at the same rate through two charcoal tubes in parallel, one of the tubes being heated by a steam jacket. The gas escaped from the steam-heated tube at a temperature of about 90° C. and from the other tube at an average temperature of 18° C. The gasoline recovery from the hot tube amounted to 60 per cent of what was obtained from the other tube.

METHOD OF GASOLINE RECOVERY

The following methods of recovery of gasoline from the charcoal have been tried:

1—Heating with mineral oil
2—Heating with glycerol
3—Heating with steam
4—Dry heating under reduced pressure

Heating with mineral oil is the method that has been generally employed.

1. HEATING WITH MINERAL OIL—The addition of mineral oil to saturated charcoal at ordinary temperatures results in the liberation of the greater part, at least, of the adsorbed substances. This operation causes the oil to foam considerably, due to the escape of gas. The gasoline-forming constituents remain dissolved in the oil, except for the portion that is unavoidably carried off with the escaping gas. The application of heat results in the liberation of more gas and in the distillation of gasoline.

The method of procedure was to place the charcoal from one tube in a 125 cc. distillation flask and to cover the charcoal with about 50 cc. of mineral seal oil, free from low-boiling hydrocarbons. After foaming had ceased heat was applied to the flask, and the gasoline distilled and collected in the usual fashion. The gasoline ceased to distil over at a vapor temperature of about 140° C., and from this point continued heating caused the temperature to rise rapidly to the initial distillation point of the oil. Care must be taken to discontinue the distillation before the oil distils over in quantity.

The use of oils more viscous than mineral seal oil is to be avoided on account of the difficulties that arise from excessive foaming. The oil distillation method works satisfactorily, the only important objection being that a trace of oil is volatilized and carried over with the gasoline vapor, slightly affecting the amount and specific gravity of the distillate.

2. HEATING WITH GLYCEROL—Glycerol can be used as a substitute for oil in recovering gasoline from the saturated charcoal. It has the advantage over oil in that the gasoline is not contaminated with a foreign substance. It has the disadvantage of being much more expensive, an objection which can be partially overcome by recovering the glycerol for repeated use.

3. HEATING WITH STEAM—The attempt was made to distil the gasoline from the charcoal with steam, but, at the end of 30 min. heating, only one-half as much gasoline had been obtained as was obtained by the use of oil, and the method was abandoned.

4. DRY HEATING—Heating the dry charcoal was found to be unsatisfactory. In one case, a sample of saturated charcoal was heated for 2.5 hrs. under a 22 in. vacuum. The vapor temperature reached 145° C. and the temperature of the charcoal was probably as high as 200° C. for a portion of the time, and yet but 60 per cent of the gasoline content of the charcoal was removed.

PORTABLE APPARATUS FOR FIELD USE

The apparatus for using charcoal in testing natural gas for gasoline can, on account of its small bulk, be readily adapted to a portable apparatus for field use. The carrying case designed by the authors is shown in Fig. 1.

DESCRIPTION—This case is about 12 in. high, 12 in. broad, and 8 in. deep, external dimensions. It is divided into two parts by a vertical partition placed midway between the front and back of the case. The portion of the case in front of the partition provides space for an orifice meter, A, and two charcoal tubes, B, all of which are attached to the partition in the positions in which they are to be used. Suitable connecting tubes permit of passing the gas through the meter and then through the two charcoal tubes in series. The sliding door in front is removed when the apparatus is in use to render the meter and tubes easily accessible, and a small door at the left provides an opening for bringing the gas to the meter through E, and for exchanging charcoal tubes.

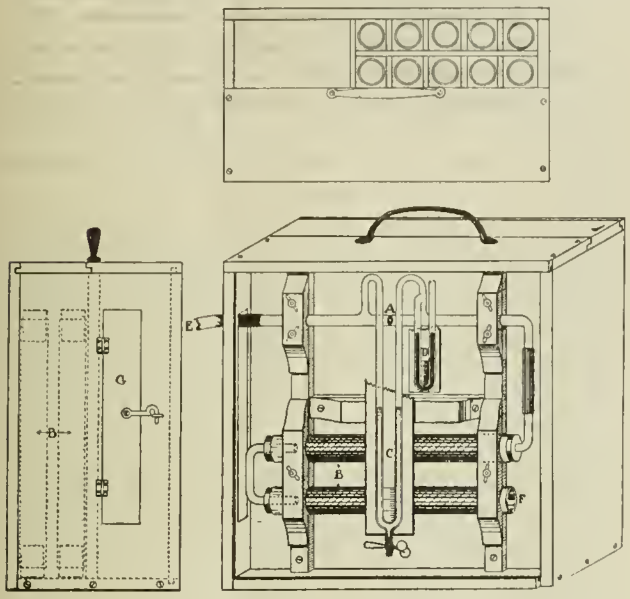

Fig. 1—Portable Testing Outfit

Access to the rear section of the case is obtained by a sliding door in its top. This portion of the case is divided into ten vertical compartments of the proper size to hold additional charcoal tubes, leaving a larger compartment at the left for additional charcoal, rubber tubing, needle valves, etc. When ready for use, with 12 tubes filled with charcoal, the weight is 14 lbs.

The orifice meter was constructed by sealing a platinum disk containing an opening 0.15 in. in diameter in the glass tube at A. The manometer C is filled with water and serves to measure the differential pressure, and manometer D, containing mercury, indicates the gas pressure in excess of atmospheric at the outlet of the orifice. The quantity of gas passing through the orifice is determined from the formula[1]

$$Q = K\sqrt{h}$$

in which Q = cu. ft. per hr., measured at 60° F., 30 in. mercury; K = constant; h = differential pressure measured when gas passes at 60° F., and under a pressure of 30 in. mercury at the orifice outlet.

If gas is passed at other than standard temperature and pressure, and if the specific gravity is different from that of air, the formula must be amplified to include these conditions, as follows:

$$Q = K\sqrt{h} = K\sqrt{h' \times \frac{P+p}{P_o} \times \frac{T_o}{T} \times \frac{G_o}{G}},$$

h' = observed differential pressure

P = barometric pressure, inches mercury, at time of gas flow

p = pressure in excess of atmospheric, inches mercury, at orifice outlet

P_o = standard pressure = 30 in. mercury

T_o = standard temperature = 520° A.

T = temperature of gas flowing through orifice, °A.

G_o = specific gravity of air = 1

G = specific gravity of gas flowing through orifice

Before use the orifice meter should be calibrated against an accurate displacement meter to determine the value of K.

The charcoal tubes shown in Fig. 1 are somewhat larger in diameter and shorter than those employed in the preliminary experiments. The internal diameter is about 1 in., and a column of charcoal about 6 in. long is placed in each tube. It is held firmly in place away from the rubber stoppers in the ends by the use of circular pieces of copper gauze wedged into position. Where desirable aluminum tubes may be substituted for the glass tubes shown in the figure.

Where field conditions are such that a glass orifice meter would probably soon be broken, a metal meter may be substituted. A brass meter of the proper size to fit into the portable case in place of the glass meter has already been constructed and installed. Its form is shown in Fig. 2.

MANIPULATION—The charcoal tubes are filled and connections made as shown in Fig. 1. Connection is made from the gas supply through a needle valve and rubber tubing to the inlet of the orifice meter, and gas is passed through the meter and charcoal tubes at a definite rate for a definite time interval. Observations are made of the duration of the test, the differential pressure, h', the gas pressure at orifice outlet, p, the barometric pressure, P, the gas temperature, T, and its specific gravity, G. The charcoal samples are taken to the laboratory where their gasoline content is determined according to the procedure already outlined.

CALCULATION OF RESULTS—From the data taken during the test, the amount of gas passed through the charcoal may be computed as outlined under the description of the apparatus.

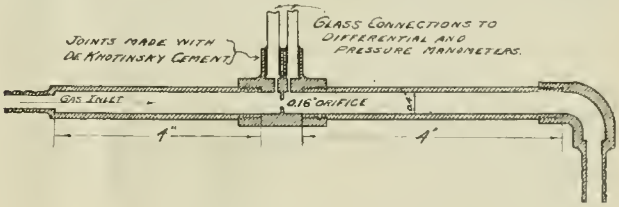
Joints made with De Khotinsky Cement
Glass Connections to Differential and Pressure Manometers.
Gas Inlet
0.16" Orifice
1"
4"

Fig. 2—Orifice Meter

The yield of gasoline expressed in gallons per M cu. ft. is then computed from the following formula:

Gal. gasoline per M cu. ft. of gas at 60° F., 30 in. mercury $= \frac{\text{Cc. gasoline recovered}}{\text{Cu. ft. gas treated}} \times 0.2642$, in which 0.2642 represents the number of gallons to one liter.

It will be noticed that the use of an orifice meter in measuring the amount of gas treated involves a knowledge of one more factor than the use of a displacement meter, *viz.*, the specific gravity of the gas. The labor involved in determining specific gravity is slight and is usually amply justified by the information that is thus obtained concerning the relationship between the specific gravity of a gas and its gasoline content as determined by the charcoal method.

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[1] T. R. Weymouth, *Trans. Am. Soc. Mech. Eng.*, **34** (1912), 1091.

It should be stated that in none of the methods in use for the determination of the gasoline content of natural gas is all of the gasoline recovered in liquid form. The charcoal method probably gives larger yields than any other method commonly employed. The highest obtainable efficiency will no doubt depend to a considerable extent on the nature of the gas being treated.

SUMMARY

I—The use of charcoal in testing gas for gasoline has been investigated. This has involved a study of the conditions under which the gas should be treated and of the conditions under which the adsorbed gasoline should be recovered.

II—A portable testing outfit has been described and directions for its use have been prepared.

THE EXTRACTION OF BITUMENS FROM MINERAL AGGREGATE[1]

By **M. R. Walczak** and **H. I. Rice**

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Received March 6, 1920

In investigations of the behavior of bituminous road materials there has been a long-felt need of some method by which a binder could be recovered for further examination from a bituminous aggregate without materially changing its character and particularly its consistency. It has been the usual practice to extract with solvents such as benzene or carbon disulfide either by digestion and decantation or in some form of extractor of which the "Forrest Hot Extractor"[2] and the "Reeve Centrifuge Extractor"[3] are representative types. These methods are entirely satisfactory for the quantitative determination of bitumen content of an aggregate or for the recovery of an aggregate for purposes of further examination. The bitumen may be recovered by evaporation of the solvent, and several methods of manipulation have been suggested,[4] but by none of them can one be sure of obtaining the bitumen in the exact condition in which it existed before extraction, particularly if it contained volatile matter which is removed with the solvent. Moreover, in the recovery of tar bitumens by the above methods the free carbon is left with the aggregate and the characteristics of the bitumen are changed accordingly.

With the above objections in mind, the authors have succeeded in developing a method and apparatus which appears to offer a large possibility of success, particularly in the recovery of fluid or semi-fluid tar bitumen without any material change in character or consistency through the recovery process.

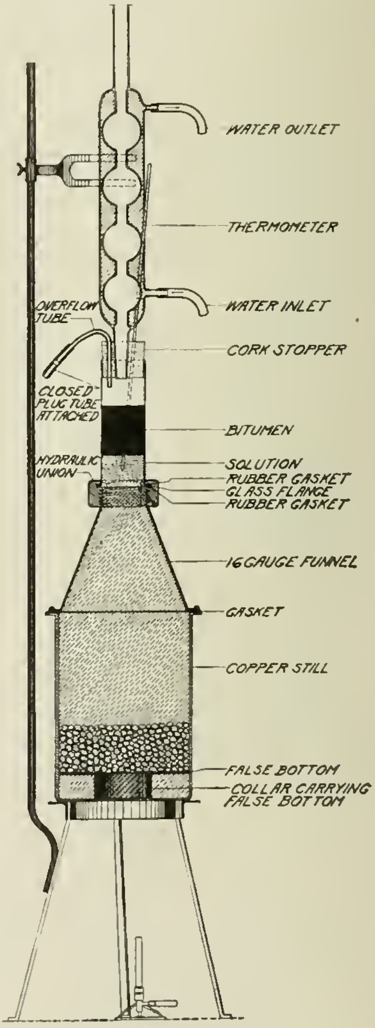
This method is based on the principle of specific gravity where the two substances, bitumen and mineral aggregate, each mutually insoluble in the other, the bitumen having a low specific gravity (approximately 1.2 at 60° F.) and the mineral matter a higher specific gravity (approximately 2.70), are separated by the use of a solution of an (approximately) inert salt of a gravity intermediate between the other two substances, thereby floating the bitumen while allowing the mineral matter to remain as a sediment.

The materials used in this work were: the mineral aggregate, consisting of a mixture of standard limestone, passing a three-quarter inch screen; a standard torpedo sand, mixed in the proportion of three to one; and aqueous sodium carbonate as the intermediate solution. This was considered the best adapted for the purpose because of its ready solubility, and because of its inertness to the tar bitumen in question, as its only probable action on the tar mixture would be solvent action upon the tar-acid content. Tests were made to determine this point by thoroughly shaking 75 cc. of the sodium carbonate solution (sp. gr. 1.27 to 1.28 at 60° F.) with 25 cc. of dry tar acids at 140° F., allowing to settle in a separatory funnel graduated to 0.1 cc. and noting any increase or decrease in either the soda solution or the upper layer of tar acids present. No variation of volume of either substance was noted, but after removal of the soda solution and its slight acidification with sulfuric acid the odor of tar acids was noted, but no layer or measurable quantity of acids was present. Actual operation of this method confirmed the view that the solvent action could be neglected.

The tar bitumen used in the experiment varied from a fluid tar to a soft pitch readily indented with the finger.

APPARATUS

An ordinary, two-liter, vertical copper still was fitted with a tightly fitting funnel-shaped lid or cover fastened to the still body with six screws and a rubber gasket. A flanged glass tube about 1.5 in. in diameter was fastened to the top of the funnel lid by means



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[1] Particularly adapted to tar bitumens.

[2] C. N. Forrest, *Proc. Am. Soc. Testing Materials*, **13** (1913), 1069.

[3] "Reeve Centrifugal Extractor: Methods for the Examination of Bituminous Road Material," by Prevost Hubbard and Charles S. Reeve, U. S. Dept. of Agriculture, Office and Public Roads, *Bulletin* **314** (1915).

[4] "Testing of Bitumens for Paving Purposes," by A. W. Dow. *Proc. Am. Soc. Testing Materials*, **1903**, 360. "The Modern Asphalt Pavement," by Clifford Richardson.

of a union pipe joint. The top of the glass tube was closed with a cork stopper fitted to a water-cooled, glass, reflux condenser, an overflow tube, and a thermometer. The interior of the still was fitted with a wire gauze (20 mesh) false bottom placed one inch above the bottom of still, resting for support on a circular collar of 20-gage metal one inch thick and 3 in. in diameter. The reflux condenser returned any of the lighter constituents to the tar bitumen present, while the overflow tube was used for the withdrawal of the bitumen when the extraction was completed.

METHOD

Two thousand grams of bituminous concrete were placed in the still and the lid fastened well, and sufficient sodium carbonate solution (sp. gr. of 1.27 to 1.28 at 60° F.) was added to bring the surface of the liquid just visible within the glass neck. Heat was applied to the bottom of still until the bitumen adhering to the mineral matter was liquefied and rose in globules and accumulated as a layer in the upper portion of the glass tube. The heat was applied gradually and care was taken not to raise the temperature any higher than necessary to float the bitumen. After all the bitumen present had accumulated the reflux condenser was washed with 10 cc. of soda solution to wash down adhering oils, after which the upper end of the reflux condenser was securely stoppered and the plugged end of the overflow tube removed. Heat was then applied rapidly to the bottom of the still to cause a rapid formation of a steam pocket below the false bottom, causing the liquid bitumen in the glass tube or neck to be ejected through the overflow which had been opened. The material was collected direct in a large test tube held at the overflow tube, and was then centrifuged for 15 min. in a Babcock milk tester. The upper layer of bituminous matter was decanted and its consistency determined by any convenient method. For very soft or fluid bitumens a float[1] test was used, having the cold bath at —5° C. and warm bath at 20° C. For heavier bitumen having a determinable melting point a regular cube melting-point (water) method[2] was used.

If any difficulty is encountered in securing the floating of the bitumen, the addition of about 100 g. of solid sodium bicarbonate to the sodium carbonate bath at the start of test will greatly aid the separation, as some bitumens, particularly the older or more weathered samples, adhere very strongly to the mineral aggregate. The sodium bicarbonate apparently overcomes this trouble by its solvent action upon the limestone when this aggregate is present, undermining the bitumen, and loosening it, when it is carried to the surface of the liquid by means of the carbon dioxide gas liberated from the sodium bicarbonate.

The following factors of this method were determined for their effect upon the consistency of the bitumen under question:

1—Accuracy of method on duplicate extractions.
2—Influence of finely suspended mineral matter present in separated bitumen upon its consistency.
3—Influence of suspended soda solution present in separated bitumen upon its consistency.
4—Quantity of mineral matter suspended in separated bitumen.
5—Does selective separation of bitumen occur, or has the first separated bitumen in a test the same consistency as the last separated portion?
6—Application of method to the two extremes of consistency of bitumen, *viz.*, fluid tar and tar pitch.
7—Is the free carbon of the tar retained by the bitumen?

The tests shown in Tables I and II were made to determine the effect of the above-mentioned factors upon the consistency of the recovered bitumen. All mixtures of bitumen and mineral aggregate were made by rotating in a 2-liter, stoppered, wide-mouth bottle to prevent evaporation of the ligher constituents of the bitumen. All mixtures consisted of 1500 g. of limestone, 500 g. of torpedo sand, and 150 g. of tar bitumen. The two bitumens used consisted of a coal-tar pitch[1] having a (cube method) melting point of 107° F. chosen as the upper extreme and a fluid tar bitumen[2] sample.

TABLE I—CONSISTENCY OF MATERIAL UNDER TEST

		Float Test Seconds at 20° C./—5° C.				Standard Water Bath M. P. ° F.	
Test No.	Material	1st Test	2nd Test	3rd Test	Average	1st Test	2nd Test
1	Original fluid-tar bitumen...........	30	30	30	30		
2	Original solid-tar bitumen...........					107	107
3	Fluid-tar bitumen after 1st extraction test...........................	38	37	37	37.3	..	..
4	Fluid-tar bitumen after 2nd extraction test, 1st portion.............	42	42	40	41.3	..	..
5	Fluid-tar bitumen after 2nd extraction test, last portion.............	46	42	45	44.3	..	..
6	Original fluid-tar bitumen (saturated with soda solution and centrifuged).	31	31	32	31.3	..	..
7	Original fluid-tar bitumen (with addition of 2 per cent mineral matter)[1]..	35	35	33	34.3	..	..
8	Original fluid-tar bitumen (with both soda solution and mineral matter added and centrifuged)...........	35	34	35	34.6	..	..
9	Solid-tar bitumen after 1st extraction test...........................	..	..	..	..	108	108
10	Solid-tar bitumen after 2nd extraction test...........................	..	..	..	..	108	108.5
11	Solid-tar bitumen after addition of mineral matter and soda solution and centrifuging.................	..	..	..	..	108.5	107.5

[1] 2 per cent mineral matter consisting of powdered limestone passing a 200-mesh screen was used here, as this is approximately the quantity found in the extracted bitumen, which on analysis was found to consist almost entirely of limestone passing a 200-mesh screen, very likely present from the limestone dust produced during the mixing of the bitumen and mineral aggregate.

TABLE II—INSOLUBLE MATTER IN BENZENE, FREE CARBON AND ASH CONTENT OF MATERIALS UNDER TEST

				Approximate Analysis of Ash	
Test No.	Total Insol. Matter in Benzene[1] Per cent	Free Carbon (Insol. Matter in Benzene minus Ash) Per cent	Ash[2] Per cent	Sodium Carbonate Per cent	Sand, Etc. Per cent
1	16.61	16.43	0.18	Normal Ash	Coal Tar
2	22.86	22.64	0.22	Normal Ash	Coal Tar
3	18.87	16.13	2.74	30	70
4	17.01	15.69 (Av. 16.40)	1.32	20	80
5	18.71	17.12	1.59	20	80
9	22.90	21.62 (Av. 22.39)	1.28	20	80
10	24.63	23.16	1.47	30	70

[1] J. M. Weiss, *Loc. cit.*, Test B7.

[2] Test B9.

DISCUSSION OF RESULTS

A comparison is here shown between the original material and the same under the influences of the various substances with which it is liable to contamination during the application of the method. The influence of soda solution is found to be but slight,

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[1] "Methods of Analysis Used in Coal-Tar Industry. II—Distilled Tars and Pitches," by J. M. Weiss. THIS JOURNAL, 10 (1918), 817. Test C8.

[2] *Ibid*., Test D6.

[1] Barrett's Standard Tarvia X (road binder).

[2] Barrett's Standard Tarvia KP (for cold patching of roads).

1.3 sec., while a slightly greater influence is shown by contamination with 2 per cent of mineral matter. The combined effect of mineral matter and soda solution is found slightly higher than that of the mineral matter alone, but not quite the sum of both. There seems to be some selective separation of bitumen as shown under Consistency Tests 4 and 5, which, however, will be reduced some under the application of the method as it is aimed to extract all of the bitumen, not half; when the extraction is completed any bitumen adhering to the mineral aggregate would be but a small percentage. By taking an average of Tests 4 and 5 (consistency), 42.8, and comparing it with Test 3 a comparison is obtained of the accuracy of the test, which in this instance was 5.5 sec., which seems reasonably close when it is seen that the float test itself under these conditions gives a variation of 4 sec.

The "Insoluble in Benzene" tests clearly demonstrate that the free carbon content of the bitumen is not altered to any appreciable extent by the application of the method.

The centrifuge method for the removal of the soda solution was adopted because of its ease of application. With the regular method of dehydration[1] there was a very great tendency to foam, and a possible loss of lighter constituents.

CONCLUSIONS

While the above tests were not as elaborate as desired, they indicate that the method would prove sufficiently accurate for the purpose for which it was designed. It is more rapid than many other methods, and the tar bitumen is separated from its mineral aggregate in substantially its true state as existing in the mixture.

The increase in consistency of the extracted bitumen is due largely to contamination and not to loss of constituents which with proper care can be reduced to a minimum; although there does seem to be some slight solvent action of the soda solution as evidenced by its change to a reddish brown solution.

Such satisfactory results were obtained by the application of this method to the extraction of tar bitumens, that there is no doubt in the authors' minds but that it would prove equally well adapted to the extraction of asphaltic binders from their mineral aggregate, perhaps not exactly as used here, but with some slight modification of the solution, dependent upon the character of the asphaltic material. This, of course, would require some further work which was not undertaken at this time.

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[1] Test B3.

THE ACTION OF ULTRAVIOLET LIGHT ON THE YEAST-LIKE FUNGI—I

By Bertram Feuer and F. W. Tanner

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Received March 26, 1920

The effect of light on both a variety of microbial organisms and chemical reactions has received considerable study. Berthelot and Gandechon,[1] Kailau,[2] Thiele,[3] and Lesure[4] have demonstrated the effect of ultraviolet rays in causing polymerization or decomposition of chemical compounds. Ostromisslenski[5] showed that vinyl bromide can be polymerized by ultraviolet light in a few hours to cauprene bromide. Similarly, Pribram and Franke[6] found that freshly distilled formaldehyde being exposed to ultraviolet rays for some time contains a substance identified as glycol-aldehyde. Studies by Buchta[7] show that light prevents the germination of cells. He also finds that yeast cells exposed to ultraviolet light for 10 sec. do not germinate and exposure for 3 min. kills the cell. Stiner and Abelin[8] found hemolytic amboceptors, diluted 1 : 100, to be destroyed in 10 min. Likewise Hartoch, Schürmann and Stiner[9] found diphtheria toxin to be weakened by exposure to the rays. Agulhon[10] and Chaulpecky[11] studied the action of ultraviolet rays on enzymes which were shown to be rendered inactive. Amylase and invertin are exceedingly sensitive to them, and albumin is coagulated by their action. Further, Chamberlain and Vedder[12] find amebae existing in water supplies, whether motile or encysted, very easily killed on comparatively short exposure to the rays. Von Recklinghausen[13] gives considerable data on the bactericidal activity of ultraviolet light together with its adaptability in the purification of water.

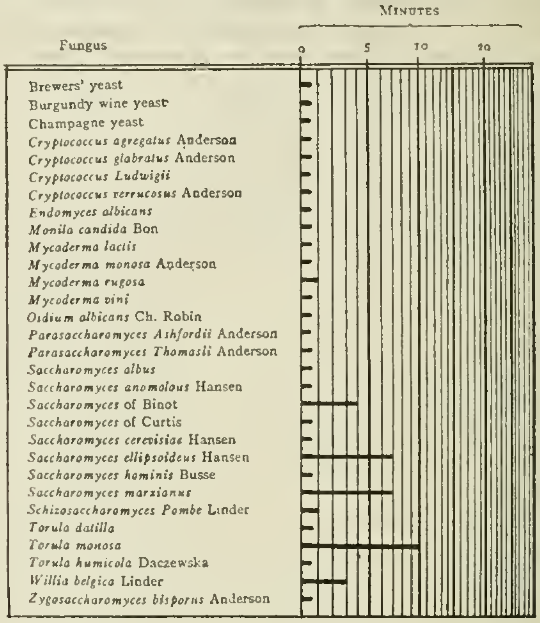

Fig. 1—Time of Survival of Each Organism after Exposure to Ultraviolet Light

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[1] *Compt. rend.*, **163** (1911), 383.
[2] *Monatsh.*, **34**, 1209.
[3] *Z. angew. Chem.*, **22** (1909), 2472.
[4] *J. pharm. chimie*, [7] **1** (1910), 569.
[5] *Chem.-Ztg.*, **36** (1912), 415.
[6] *Monatsh.*, **33**, 415.
[7] *Centr. Bakt. Parasitenk., II Abt.*, **41** (1914), 340.
[8] *Z. Immunität.*, **20** (1914), 598.
[9] *Ibid.*, **21** (1914), 643.
[10] *Ann. inst. Pasteur*, **26** (1912), 38.
[11] *Zentr. Biochem. Biophys.*, **14** (1912), 927.
[12] *Philippine J. Sci.*, **6B** (1911), 383.
[13] *J. Frank. Inst.*, **1914**, 681; *J. Am. Water Works Assoc.*, **1** (1914), 565.

As shown by the foregoing, ultraviolet rays have received extensive application in a variety of ways and considerable data is now available from these investigations. To add to the present state of knowledge of the subject this work was undertaken in order to get a preliminary idea of the length of time necessary for the survival of a variety of yeast-like fungi upon exposure to the ultraviolet rays. Kny and Lohman[1] are the only investigators who have studied the effect of light on yeast cells, but their interest was mainly in the matter of germination. Further, they did not investigate the germicidal effect of the ultraviolet light on the types of organisms taken up here.

A variety of thirty (old) cultures of yeasts listed in the appended table, Fig. 1, were used for this investigation. The technique employed was primarily as follows:

A water suspension of the organism was made by taking a standard loop full of the growth from a dextrose agar slant and distributing it in a tube containing 9 cc. of sterile water. In turn these 9 cc. suspensions were placed in small-sized Petri dishes, placed in the position indicated in the accompanying sketch, Fig. 2, and exposed to the action of the rays.

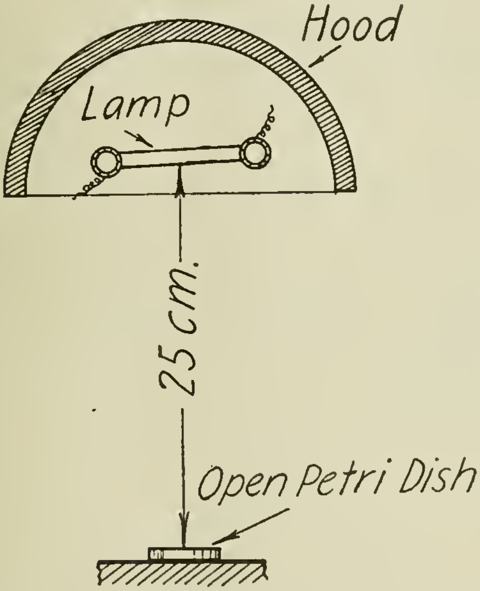

Fig. 2—Apparatus Used in Determining Time of Survival

The source of ultraviolet light used was from a R. U. V. quartz mercury vapor lamp operating on 110 volts. The suspension in an uncovered Petri dish was placed directly under the lamp, at a distance of 25 cm. By means of a thermometer placed beside the dish during the experiment the temperature was noted to vary between 30° and 40° C. At intervals of one minute until 10 min. were reached and then at intervals of 5 min. one loop full of the suspension was removed and used to inoculate a dextrose agar slant which in turn was incubated at 37° C. for a period of 3 days. The presence or absence of growth after this period of incubation determined whether or not the cells were killed. Precautions were taken to have the suspension as homogeneous as possible, to secure representative samples, and to keep all conditions uniform throughout all the experiments. Blanks were used in all cases to check in each experiment.

The results obtained are presented diagrammatically in Fig. 1. The vertical lines indicate intervals of one minute. The horizontal line drawn for each organism shows the length of time the organism survived. Twenty-three out of 30 organisms were killed before one minute elapsed, two survived one minute, one survived three minutes, one four minutes, two seven minutes, and one ten minutes. This shows that the majority of the yeast-like fungi are not any more resistant to ultraviolet light than the ordinary water bacteria.

CONCLUSIONS

From the data obtained it is evident that yeast cells are not very resistant to ultraviolet light.

Possibilities are seen for the use of ultraviolet light in controlling the development of yeast cells in the industries.

Further work is planned to obtain quantitative data and study the effects of the light on the cells suspended in a variety of media.

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SOME ANOMALIES IN THE SOLIDIFICATION POINT OF TRISTEARIN[1]

By Ben H. Nicolet

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In common with certain other triglycerides, tristearin shows the phenomenon of a double melting point, thus apparently existing in two forms. The melting point of the stable form, obtained by crystallization from any solvent, or by keeping the unstable form, is variously given as 71.6° to 72.2°. After barely melting, it is said by Bömer to resolidify at 70°. Heated a few degrees above its melting point, tristearin solidifies on cooling to the unstable form, which is stated to melt in a capillary at about 55°, and on further heating to resolidify and show the melting point of the stable modification. The same change to the stable form occurs on standing for some hours at room temperature.

Curiously enough, in spite of the rapidity with which conversion into the stable form takes place at higher temperatures, the solidification point usually reported for tristearin is about 56°,[2] apparently that of the unstable form.

The usual method of determining solidification points of commercial fats is to let a considerable quantity (about 30 g.) solidify in a wide test tube (titer tube) placed in the neck of a bottle for an air jacket, and to read the maximum temperature registered by a thermometer placed in the fat. A sample of Kahlbaum's tristearin, not specially tested as to purity, gave a rather surprising result. Solidification, with accompanying rise of temperature, began at 53.8°. The temperature rose quite normally for about 10 min. and nearly stopped at 63.5°. After 2 or 3 min., during which the rise was only 0.1° per minute, the temperature began to go up rapidly again, reaching a maximum at about 69° (Curve I, and Column I of Table 1).

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[1] *Ber. botan. Ges.*, No. 3, **2** (1884).

[1] Presented in part at the 52nd Meeting of the American Chemical Society, Urbana, Ill., April 18 to 21, 1916.

[2] R. Kremann and R. Schoulz, *Monatsh.*, **33** (1912), 1063. The quantities with which they worked are not stated, but even with "larger quantities" the results were reported to be the same.

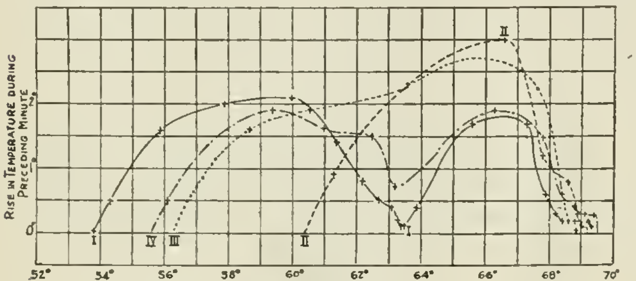

Fig. 1—Solidification of Tristearin

Table 1—Temperature Readings[1] by Minutes in Solidification Points of Tristearin

I Not seeded	II Seeded at 61°	III Seeded at 57°	IV Seeded at 56°
53.8	60.4	56.3	55.6
54.3	61.3	57.1	56.1
55.9	63.6	58.7	57.5
57.9	66.6	60.6	59.4
60.0	67.8	62.7	61.0
61.4	68.6	65.4	62.5
62.2	68.9	67.7	63.2
62.7	69.0	68.4	64.4
63.1	69.2	68.6	66.3
63.3	69.3	68.8	67.8
63.4	69.4	69.0	68.4
63.5	69.4	69.1	68.8
63.9	....	69.2	69.1
65.6	....	69.2	69.4
67.3	....	....	69.5
67.9	....	....	69.5
68.2	....	....	....
68.4	....	....	....
68.6	....	....	....
68.8	....	....	....
68.85	....	....	....
68.9	....	....	....
68.9	....	....	....

[1] Each type of these solidification points was, of course, repeated a number of times, so as to make sure that the numbers here given are thoroughly characteristic.

This result could be duplicated at will. In fact, the only way in which the low results usually reported could be even approximated was to use a narrower tube with a smaller quantity (7 to 8 g.) of substance, when radiation losses would prevent the realization of the temperature of rapid transformation.

Seeding the melt with the stable form (solid tristearin which had not been recently melted) also led to interesting results. Seeded above 60°, the curve showing rate of temperature rise showed no minimum, and there was no indication of the appearance of the unstable form (Curve II, and Table 1, Column II). Seeded in the neighborhood of 56° or lower, there was always a noticeable minimum in the rate of temperature rise, in the neighborhood of 63°; but this temperature would in such cases be passed much more rapidly than without seeding. Of this behavior, Curve IV is typical. Curve III shows an intermediate behavior where there is an obvious tendency to show a minimum which is yet not realized.

These results are interesting in themselves. If one tries to interpret them, they seem to indicate that:

1—By seeding with the stable form, liquid tristearin may be made to solidify without the intervention of the "unstable form," when the temperature is above 60°.

2—When the temperature is below 56°, the unstable form always appears, even when crystallization is started by seeding with the stable form.

3—For a range of a few degrees above the melting point of the unstable form, its rate of transformation is quite slow. This rate of change becomes rather rapid at a somewhat definite temperature, which for the sample of tristearin examined was a few tenths over 63°.

It will be seen readily that all triglycerides which show a double melting point need not of necessity show this "double solidification point" when crystallizing spontaneously. The necessary condition will be that the solidification of the unstable form shall raise the temperature sufficiently to realize the temperature of rapid transition to the stable form. Cases where this condition is not fulfilled may perhaps sometimes be recognized by the fact that in them seeding with the stable form will give a final maximum temperature several degrees higher than otherwise obtained.

BEHAVIOR OF CERTAIN HYDROGENATED OILS

Such behavior has not yet been noted with a pure triglyceride, but is rather well illustrated by a sample of crude soy-bean oil which was hydrogenated quite completely. The iodine number of the product, which unfortunately was not determined, could hardly have been more than 2 or 3. The oil contained 8.1 per cent of saturated acids other than stearic.

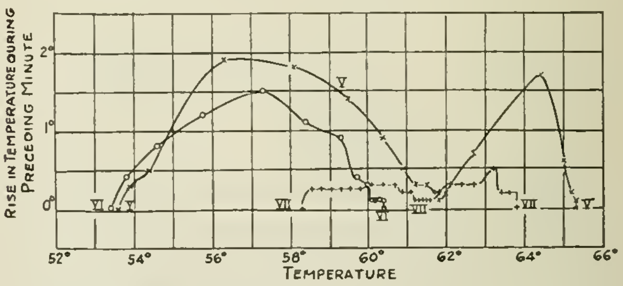

Fig. 2—Solidification of Hydrogenated Linseed and Soy-Bean Oil

Taken in the ordinary way, this oil showed consistently a solid point of 60.4°. Seeded with the stable form, a curve was obtained showing a minimum rate of temperature rise at 61° to 61.5°, and a solid point of 63.8° (Curves VI and VII, and corresponding columns in tables). In other words, the transformation of the tristearin to the stable form does not take place rapidly enough to be recognized by this method below 61°, while on the other hand the other glycerides present depress the solidification point of the unstable form sufficiently so that, without seeding, this temperature is not reached. Seeding produces a rise in the maximum temperature reached during solidification of 63.8° — 60.4°, or 3.4°.

TABLE 2—TEMPERATURE READINGS BY MINUTES IN SOLIDIFICATION POINTS OF HYDROGENATED OILS

V	VI	VII
Hydrogenated Linseed Oil	Hydrogenated Soy-Bean Oil	Same, Inoculated with Stable Form
53.6	53.4	58.3
53.9	53.8	58.55
54.4	54.6	58.8
56.3	55.8	59.05
58.1	57.3	59.3
59.5	58.4	59.55
60.4	59.3	59.8
60.9	59.7	60.1
61.2	60.0	60.4
61.5	60.1	60.7
61.7	60.2	60.9
61.8	60.3	61.1
62.0	60.4	61.2
62.7	60.4	61.3
64.4	....	61.4
65.0	....	61.5
65.2	....	61.6
65.3	....	61.8
65.3	....	62.1
....	....	62.4
....	....	62.7
....	....	63.2
....	....	63.4
....	....	63.6
....	....	63.8
....	....	63.8

A refined linseed oil, hydrogenated to a titer of 65.9° and an iodine number of 2.7, gave a solid point of 65.3°, without seeding. Curve V shows a minimum at 61.7°. The solid point in this case was of course not raised by seeding. This oil contained, besides 3 per cent oleic acid as indicated by the iodine number, 7.5 per cent of palmitic and myristic acids among its glycerides.

A cottonseed oil containing 28 per cent palmitic acid could not, even after hydrogenating to zero iodine number, be made to show any evidence of double solidification point.

In conclusion, attention may be called to bayberry tallow and Japan wax (as this is a glyceride, the name wax is unfortunate), these two fats containing unusually high percentages of tripalmitin. Commercial specimens at hand showed decided, but not altogether definite, indications of double solidification point. Both crystallize slowly even for glycerides, so that the radiation losses are probably large.

Bayberry tallow gave capricious solid points by the usual method, varying from 53.7° to 57.4°. On seeding with the stable form, values of 58.0° to 58.3° were obtained.

Japan wax has been reported as showing a double melting point. The sample at hand was quite rancid. Its solid point, unseeded, was 43.9°. Seeded with some shavings of the solid material that had not been melted for a long time (presumably, therefore, the stable form) the temperature climbed slowly to 46.7° to 47.3° in various trials. Much the same effect could be obtained by surrounding the bottle which served as air-jacket with a bath of water at 35° to 40°. The solid point then reached temperatures of 46.0° to 48.2°. These last two cases behave quite differently from those described before since the rate curve for temperature rise shows no decided minimum, and solidification is so slow that the final maximum temperature is far from constant. It is therefore left undecided for the present whether the same phenomenon of double solidification is here at work.

CELLULOSE PHTHALATE: ITS PREPARATION AND PROPERTIES[1]

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The Aircraft Production program required for treatment of the fabric of the planes enormous quantities of cellulose acetate "dope." The preparation of this commodity required acetic anhydride and acetic acid for the manufacture of cellulose acetate; and as solvents acetic esters, higher ketones, and acetone. The last-named compound was urgently needed by the Ordnance Department, also as a solvent for cellulose nitrates used in explosives. It so happens that the principal source of all of these materials is acetate of lime. Because of this dearth of acetate of lime products, other derivatives of cellulose were studied with a view to preparing a compound which would not require these products either in its preparation or as solvents. Phthalic anhydride of high purity being available in commercial quantities at a reasonable cost, studies were made of the preparation of cellulose esters of phthalic acid.

The chemical inertness of cellulose, and the high melting point of phthalic anhydride (130.84° C.) make direct esterification difficult. Cotton cellulose is in a physical condition which resists the manipulation desirable for reaction, and the temperature at which phthalic anhydride is liquid is sufficiently high to cause the complete destruction of the cellulose, especially in the presence of the necessary catalyst. For this reason a modified cellulose, designated by the patentee[2] as "hydrocellulose," was used.

EXPERIMENTAL

Ten grams of the modified cellulose were placed in a glass-stoppered flask and a solution (at 70° C.) of 30 g. phthalic anhydride and 2.5 g. fused zinc chloride in the least possible quantity of diethyl phthalate added, thoroughly mixed, and maintained, with occasional stirring, at a temperature of 70° C. for 24 hrs. The product was washed free from solvent and reagents, and dried *in vacuo* at a temperature not exceeding 70° C.

A sample of the product saponified by heating to 80° C. for 2 hrs. with ten times its weight of a 2 *N* solution of potassium hydroxide in 50 per cent alcohol, showed a content of combined acid not large, but unmistakable. This was not due to the difficulty of washing out the diethyl phthalate, for the product resulting from an experiment similar, except for the omission of the phthalic anhydride, gave no combined acid titer, although it gave a fluorescein test on heating with resorcinol and fused zinc chloride. Nevertheless, the sample of cellulose phthalate used for analysis was prepared in acetic acid solution, the procedure being the same as described above, except for the replacement of the diethyl phthalate by 100 cc. of glacial acetic acid.

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[1] This work was undertaken at the request of the Bureau of Aircraft Production

[2] U. S. Patent 679,204. Prepared by passing chlorine into glacial acetic acid until it is colored yellow, and treating cotton with about 6 times its weight of this acid solution at 70° C. for one to three hours. The cotton has then been reduced to an impalpable dust, and is washed free from acid and dried.

It may be objected that this requires as much acetic acid as would the preparation of cellulose acetate; but the acetic acid does not combine with the cotton, and can be recovered. It is to be expected that substitutes for acetic acid in this treatment can be found, since it serves solely as a solvent.

Similar considerations justify the use of acetic acid or its derivatives in some other parts of the experimental work here described.

Carbon and hydrogen were determined in three samples:

	Observed I	II	III	Calculated for $C_{56}H_{92}O_{47}$
C............	44.45	44.20	44.30	44.33
H............	6.47	5.98	6.15	6.07
O............	49.08	49.82	49.55	49.60

The calculated values are for $C_8H_4O_3.8C_6H_{10}O_5.4H_2O$ = $C_{56}H_{92}O_{47}$, corresponding to a molecular weight of 1516.

The combined acid was determined by hydrolyzing with alcoholic potassium hydroxide as described above, titrating the excess alkali with 0.940 N hydrochloric acid and subtracting this titer from that of a volume of alkali equal to that originally taken for the saponification. Two samples contained acid, per gram of cellulose phthalate taken, equivalent, respectively, to 1.42 cc. and 1.37 cc. of 0.940 N hydrochloric acid.

Multiplying these volumes (in liters) by the normality of the hydrochloric acid and by the molecular weight, 1516, obtained by combustion analysis:

$$0.00142 \times 0.940 \times 1516 = 2.021$$

$$0.00137 \times 0.940 \times 1516 = 1.951$$

which agrees well with the value, 2, for one molecule of the dibasic phthalic acid per molecule of cellulose phthalate.

As cellulose acetate and phthalic anhydride have common solvents it was hoped that a sample of cellulose phthalate for the study of the properties of that substance might be made by their interaction, but after heating for 24 hrs. in the presence of zinc chloride the cellulose acetate was recovered practically unchanged.

Replacing the zinc chloride by sulfuric acid, or the cellulose acetate by cellulose nitrate, did not change this result.

As was to be expected, when normal cotton cellulose was employed even less action was obtained than with the modified cellulose.

PROPERTIES OF CELLULOSE PHTHALATE

Samples of the cellulose phthalate were treated, in the cold and at the boiling point of the solvent, with acetone, chloroform, ethyl acetate, benzene, carbon tetrachloride, toluene, pyridine, acetic acid, the xylenes, tetrachloroethane, aniline, ether, nitrobenzene, and diethyl phthalate, both alone and mixed with various proportions of ethyl alcohol, but in no case was any residue found on evaporation. In Schweitzer's reagent a small amount passed into solution.

An attempt was made to increase the solubility by heating to 75° C. with zinc chloride in 50 per cent acetic acid, but without success.

SUMMARY

1—Cellulose, or at any rate modified cellulose, forms a difficultly soluble phthalic acid ester.

2—The presence of a condensing agent, such as zinc chloride, is necessary.

3—Diethyl phthalate is as good a medium for this reaction as acetic acid, but is not a phthalating agent.

4—The optimum temperature for esterification is 70° C.

5—The degree of phthalation is not increased by heating longer than 24 hrs.

6—Phthalic anhydride will not displace the acetate radical from cellulose acetate or the nitrate radical from cellulose nitrate.

7—The amount of phthalic acid introduced is equal to one mole to eight of cellulose, reckoned as $C_6H_{10}O_5$.

THE RELATIVE IMPORTANCE OF SOME COLORING MATTERS IN CANE JUICES AND SIRUPS[1]

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The results of the investigations so far carried out in this laboratory on the color of sugar-cane products[2] have shown that certain polyphenol compounds occurring in the cane play a very important part in color formation. We have found that the color of raw cane juice is largely determined by three factors, *viz.*, tannin, iron salts, and oxidizing enzymes. Juice extracted in the absence of iron soon turns brown, owing to the effect of the oxidases on the polyphenols. If iron salts are also present, as is the case when the juice is extracted by iron mills, the juice assumes a greenish color due to ferric tannin compounds. Thus a juice may exhibit all the different shades between brown and green, according to the proportion of tannin and iron it contains. The color of the raw juice is further affected by the water-soluble coloring matters of the rind of the cane, which are also polyphenols in the wider sense, belonging to the anthocyanin group. We have shown that mill juice from purple canes may be 50 per cent darker than that from green canes. The iron-greening, water-soluble polyphenol of the cane has been found by us to be a tannin, closely resembling oak-tannin, and derived from pyrocatechol. In the sugar-house tests carried out during the grinding season of 1918 to 1919, we established the fact that the depth of color of all our products, juices, sirups, sugars, and molasses, rises and falls with the amount of ferric polyphenol compounds contained in them. It was thus proved that these combinations play a very important part in the color of our products, but the question still remained how much of the total color was due to them, and how much to other well-known coloring matters, the presence of which had been established before. These coloring matters may be grouped in three classes:

(1) The coloring matters in the rind of the cane, belonging to the chlorophyll and anthocyanin groups, and evidently also associated with a tannin; the chlorophyll as such does not seem to be of much importance, being insoluble in cane juice.

(2) The incrustating coloring matter of the fiber, termed saccharetin by Steuerwald; this is also a polyphenol derivative.

(3) The products formed by the decomposition of sugars,

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[1] Presented at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 2 to 6, 1919.

[2] Louisiana Experiment Station, *Bulletins* **157** and **165**; This Journal, 10 (1918), 814; **11** (1919), 1034.

especially reducing sugars, under the influence of heat alone, or by the simultaneous effect of alkalies, particularly in the presence of amino acids.

These three groups of coloring matters have been known for a long time, but practically nothing has been ascertained concerning the exact extent to which each of them contributes to the color of our various sugar-house products. We have planned to make a special study of this question in order to arrive at a basis for the scientific interpretation of the problems of the Louisiana sugar industry. The present-day consumer in the United States demands white sugar, and light-colored sirups and molasses. It is perfectly true that with manufacturing methods now in vogue a certain quantity of high-grade white sugar is being produced directly from the cane in various countries, notably in Java and in Louisiana. But the problems connected with this subject are not the same in these two countries. Java is striving to produce the largest possible quantity of white sugar per ton of cane, the quality of the resultant molasses being immaterial. Harloff[1] has pointed out in a recent article that the acid thin juice process, with heavy sulfuring of the sirup, serves admirably for this purpose, because the sirup sulfitation prevents the iron contained in the massecuite from entering the sugar crystals and thus from producing the dark color caused by ferric polyphenol compounds. But the molasses obtained by this process is certainly unfit for human consumption, and for this reason the process would not help us much in solving our problem in Louisiana. Here we must endeavor to produce the largest possible quantity of white sugar consistent with the production of such a quantity of high-grade molasses that the combined output will bring the largest financial return. In order to do this, we must not merely prevent the presence of iron in the sugar alone, but must decrease both iron and all other coloring matters in the massecuite to the lowest possible point. It therefore becomes a necessity to have an exact knowledge of the nature and proportions of the various factors contributing to the color of our products.

EXPERIMENTAL METHODS

There are two ways in which this latter problem might be attacked: either we must devise methods for the quantitative determination of all the coloring matters enumerated above, or else we may prepare artificial products in which the different coloring matters are added by themselves and in combination, and determine their effect on the color of the products. The first method would no doubt be preferable from the scientific standpoint, but it is fraught with great practical difficulties. According to Browne, tannin, coloring matter, etc., amount altogether to only 0.01 per cent of the weight of the cane juice; and even if there were more than that figure, as is the case in the denser products, it would be a very difficult, and, to say the least, a very tedious procedure to devise quantitative methods for estimating each one of a number of different coloring matters which are but imperfectly studied and the sum total of which is so small. We have therefore decided to attack the problem in the second, synthetic way, and this article deals with the effect of two groups of coloring matters, the decomposition products of sugars by heat, in the presence and absence of other impurities, and of the iron-greening, water-soluble tannin of the cane. For experimental reasons we have so far carried the work only from raw juice through clarified juice to sirup, reserving work on the denser products for another series of experiments.

COMPOSITION OF ARTIFICIAL JUICES—The composition of the artificial raw juices was made to conform as closely as possible to that of an average Louisiana cane juice. In the first series of tests we used a 12 per cent sucrose solution to which enough aconitic acid, the principal acid of sugar cane, was added to bring the phenolphthalein acidity to 0.015 *N*, that is, 1.5 cc. 0.1 *N* per 10 cc. of solution, which is about the average acidity of a Louisiana cane juice. In the second series of tests we used in addition to the sucrose 2.1 per cent of invert sugar; this is near the maximum figure found in a juice, but it was used to accentuate any effect of its decomposition products. In the third series there was further added 0.067 per cent of asparagine, exactly neutralized with potassium hydroxide, and in the fourth series we increased this still further by 0.133 per cent of aspartic acid, also neutralized with potassium hydroxide. The sum of asparagine and aspartic acid represents the quantity of protein cleavage products occurring in our juices. In the fifth series there was added to the previous constituents a quantity of iron-greening tannin prepared from cane, corresponding to 0.0167 per cent of gallotannic acid. This is about one-half of the total polyphenol compounds we found in the raw juices of 1918, and in this way we made allowance for other polyphenols occurring besides the iron-greening tannin in raw juice. It will be noted that no ash constituents were added except the potassium hydroxide, and the sulfur and lime used in clarification. From all we know on this subject, only iron and organic salts of potash and lime affect the color of the products.

CLARIFICATION OF JUICE—The raw juice prepared in each of these five series was clarified by five different methods based on those which are used in actual factory practice. In the first the juice was treated with sulfur dioxide in the cold until an acidity of 0.06 *N* was reached, and at once limed back to an acidity of 0.01 *N*. This process is quite generally employed in white sugar manufacture in Louisiana. The second method of clarification consisted in sulfuring to 0.06 *N* acidity and liming back to 0.002 to 0.003 *N* acidity. This procedure is practiced in raw sugar manufacture in Louisiana, except that the sulfuring is usually not carried so far in this case; however, we used the same quantity of sulfur dioxide as in Method 1, to have a comparable basis. In the third method the juice was sulfured to 0.06 *N* acidity, and then treated with lime until it showed an alkalinity of 0.002 to 0.003 *N*. This was done to study the effect of a slight excess of lime in the presence of sulfites. In the fourth and fifth methods only lime was used, as is generally done in raw sugar manufacture in the tropics, the lime being added in Method 4 to an acidity of 0.002 to 0.003 *N*, as in Method 2, and in Method 5 to an alkalinity of 0.002 to 0.003 *N* as in Method 3.

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[1] *Louisiana Planter*, **63** (1919), 61.

After the addition of sulfur and lime, or lime alone, the juice was boiled and filtered, enough water being added to make up for evaporation. The product obtained in this way corresponds to the clarified juice of the factory. A part of this clarified juice was then in each case evaporated under a partial vacuum at about 70° to one-fifth, and then made up again to the original volume in order to make all the color determinations at equal concentrations.

In the way just described samples of raw juice, clarified juice, and sirup were prepared in 25 different "runs." All of these runs were then repeated, adding 0.002 per cent of iron in the form of ferric chloride to the raw juice, this being about the maximum of total iron found during the last grinding season. In the first series of raw juices, containing sucrose alone, we added less ferric iron, but also some metallic iron to imitate the effect of the iron of the mill. More metallic iron was added to the clarified juice before boiling down to sirup; but it was found that the quantities of iron taken up varied so much that the metallic iron was left out in the other four series.

ANALYSIS OF PRODUCTS—Each product, raw juice, clarified juice, and sirup, from every run, was, after filtration through filter paper, subjected to the ordinary sugar-house analysis, determining Brix, sucrose by double polarization, reducing sugars by the volumetric method, and acidity or alkalinity by titration, using phenolphthalein as indicator. Besides these, we also measured the total depth of color by the Hess-Ives tint-photometer. The Stammer colorimeter, used so extensively in beet work, is not suited for our purpose, because the tints found in our juices are entirely unlike those of the normal color plates in that instrument. The Hess-Ives tint-photometer was the only practicable instrument which we could obtain at the time. We have already pointed out in former articles that for precision work this instrument in its present form needs to be greatly improved; but, although the limits of error are rather large, we believe the results to be sufficiently accurate for our purpose, and they are certainly much more useful than a mere description of the tint and depth of color as appearing to the eye. The use of the spectro-photometer would have consumed too much time in this work, where a complete run with all its attendant analytical work had to be finished in one day, because these products do not keep for any length of time. In all the runs where iron and where polyphenols were used these were also determined colorimetrically with the aid of the same instrument, and it has been found quite useful for this purpose, as long as methods of higher precision have not been worked out. In such products as we have to deal with, and which are often themselves highly colored, the use of ordinary colorimeters is out of the question. Ferric iron was determined by the color produced with ferrocyanide in acid solution, the ferrous iron with ferricyanide, and the polyphenols by Allen's color reaction produced by ferricyanide and ammonia.

The regular sugar-house analysis of our products was made in order to make certain that the clarified juices and sirups did not present any abnormal composition as compared with the regular factory products. It was found that the sucrose remained constant, within the limits of error, in all cases. The extent of the decomposition of reducing sugars was practically nil in all methods where lime was not added to alkalinity, and even in the alkaline series the quantity decomposed exceeded in no case 7 per cent of that originally present. It is unnecessary to give all these figures in detail, especially inasmuch as Van der Linden[1] has published an extensive investigation on this subject, and as we are more particularly interested here in the color due to the products in question and its proportion to other coloring matters.

A part of every raw juice, clarified juice, and sirup was also treated with one gram of Norit per 100 cc., and color, ferrous iron, ferric iron, and tannin determined in the filtrates. It will not be necessary here to discuss all the results in detail, and we shall mention only those obtained with the darkest products, those of Series V, in the presence of iron. At an acidity of 0.015 *N*, the Norit removed an average of 89 per cent of total coloring matter; at an acidity of 0.002 to 0.003 *N*, about 79 per cent, and near neutrality about 73 per cent. It was also found that this reduction in coloring matter went hand in hand with a corresponding decrease in ferric iron and tannin, while the ferrous iron was not reduced to nearly as great an extent as the former two.

DISCUSSION OF ANALYTICAL RESULTS

The results of our analytical work are given in the accompanying tables, one for each double series. The upper half of the table contains the results for the runs without iron, and the lower half those for the runs with iron. The first column of figures gives the acidity or alkalinity in cc. 0.1 *N* per 10 cc. of solution, the minus sign denoting alkalinity. The next three columns show the readings in the Hess-Ives tint-photometer, always using equal volumes of liquid in the same dish, under the red, green, and blue glass, respectively. The fourth column gives the total depth of color in degrees of the instrument, calculated from the three readings, according to information furnished by the designers. In the next column are given the color units corresponding to the degrees found, on the basis of a curve constructed by plotting known concentrations of a molasses solution against the corresponding readings of the instrument. The following three columns give the ferric iron, ferrous plus ferric iron, and the polyphenols in parts per million (p. p. m.), the latter in terms of gallotannic acid. The last column shows the p. p. m. of the combination of ferric iron with polyphenols, calculated on the basis of certain tests which showed that when the proportion of polyphenol to iron exceeds 7 to 1

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[1] *Arch. Suikerind.*, **23** (1915), 1979; **24** (1916), 609.

Series I—Sucrose

	Acid. or Alk.	Color			Color. Total Degrees	Color Units	Ferric Iron	Total Iron	Polyphenols	Ferric Polyph. Compounds
		Red Glass	Green Glass	Blue Glass						
				A—Without Iron						
Method 1										
Raw juice	1.5	0	1	2	0.9	0.2	..	..	..	..
Clar. juice	0.9	0	1	2	0.9	0.2	..	..	..	..
Sirup	0.8	0	1	2	0.9	0.2	..	..	..	..
Method 2										
Raw juice	1.5	0	1	2	0.9	0.2	..	..	..	..
Clar. juice	0.2	0	0	0	0	0	..	..	..	..
Sirup	0.2	0	0	1	0.1	0	..	..	..	..
Method 3										
Raw juice	1.5	0	1	2	0.9	0.2	..	..	..	..
Clar. juice	—0.2	0	0	1	0.1	0	..	..	..	..
Sirup	—0.1	0	0	1	0.1	0	..	..	..	..
Method 4										
Raw juice	1.5	0	1	2	0.9	0.2	..	..	..	..
Clar. juice	0.2	0	0	0	0	0	..	..	..	..
Sirup	0.2	0	0	1	0.1	0	..	..	..	..
Method 5										
Raw juice	1.5	0	1	2	0.9	0.2	..	..	..	..
Clar. juice	—0.2	0	0	0	0	0	..	..	..	..
Sirup	—0.1	0	0	1	0.1	0	..	..	..	..
				B—With Iron						
Method 1										
Raw juice	1.5	0	0	0	0	0	9	25	0	0
Clar. juice	0.9	0	0	1	0.1	0	5.5	14.5	0	0
Sirup	0.8	0	0	0	0	0	9	27	0	0
Method 2										
Raw juice	1.5	0	0	1	0.1	0	8	39	0	0
Clar. juice	0.3	0	0	1	0.1	0	2	3	0	0
Sirup	0.3	0	0	0	0	0	2	2.5	0	0
Method 3										
Raw juice	1.5	0	0	1	0.1	0	2	7	0	0
Clar. juice	—0.3	0	0	0	0	0	0	2	0	0
Sirup	—0.1	0	0	0	0	0	0	2	0	0
Method 4										
Raw juice	1.5	0	0	0	0	0	12	37	0	0
Clar. juice	0.2	0	1	2	0.9	0.2	0	0	0	0
Sirup	0.2	0	1	2	0.9	0.2	4	0	0	0
Method 5										
Raw juice	1.5	0	0	1	0.1	0	9	21	0	0
Clar. juice	—0.3	0	0	0	0	0	T	T	0	0
Sirup	—0.2	0	0	1	0.1	0	T	T	0	0

Series II—Sucrose and Glucose

	Acid. or Alk.	Color			Color. Total Degrees	Color Units	Ferric Iron	Total Iron	Polyphenols	Ferric Polyph. Compounds
		Red Glass	Green Glass	Blue Glass						
				A—Without Iron						
Method 1										
Raw juice	1.5	0	0	1	0.1	0	..	..	..	..
Clar. juice	0.9	0	0	1	0.1	0	..	..	..	..
Sirup	0.6	0	0	0	0	0	..	..	..	..
Method 2										
Raw juice	1.5	0	0	0	0	0	..	..	..	..
Clar. juice	0.2	0	0	1	0.1	0	..	..	..	..
Sirup	0.2	0	0	0	0	0	..	..	..	..
Method 3										
Raw juice	1.5	0	0	0	0	0	..	..	..	..
Clar. juice	—0.1	0	4	6	3.4	0.8	..	..	..	..
Sirup	0	0	3	7	2.8	0.7	..	..	..	..
Method 4										
Raw juice	1.5	0	0	0	0	0	..	..	..	..
Clar. juice	0.3	0	0	0	0	0	..	..	..	..
Sirup	0.3	0	0	1	0.1	0	..	..	..	..
Method 5										
Raw juice	1.5	0	0	0	0	0	..	..	..	..
Clar. juice	0.1	0	4	9	3.7	0.9	..	..	..	..
Sirup	0.2	1	10	21	9.3	3.1	..	..	..	..
				B—With Iron						
Method 1										
Raw juice	1.5	0	0	1	0.1	0	4	6.5	0	0
Clar. juice	1.0	0	0	1	0.1	0	6	8	0	0
Sirup	0.8	0	1	1	0.8	0.2	6	8.5	0	0
Method 2										
Raw juice	1.5	0	0	1	0.1	0	6	12	0	0
Clar. juice	0.3	0	2	8	2.2	0.5	9	13	0	0
Sirup	0.2	0	3	5	2.6	0.6	7	11	0	0
Method 3										
Raw juice	1.5	0	0	0	0	0	3	5	0	0
Clar. juice	—0.1	0	4	10	3.8	0.9	7	17	0	0
Sirup	0.1	0	8	14	7.0	2.1	7	17	10	11
Method 4										
Raw juice	1.5	0	0	0	0	0	2.5	4.5	0	0
Clar. Juice	0.3	0	0	1	0.1	0	2.5	2.5	0	0
Sirup	0.2	0	0	0	0	0	2	3	0	0
Method 5										
Raw juice	1.5	0	0	0	0	0	3	5	0	0
Clar. juice	0.1	1	8	21	7.9	2.6	10	20	0	0
Sirup	0.2	7	18	34	17.4	7.0	10	20	20	23

the color maximum is reached, any excess of polyphenol not combining with the iron. In order to facilitate the interpretation of these five tables, we have arranged a sixth one, showing only the units of coloring matter in each product. In all those cases where the color actually found amounted to less than one-half unit, we have designated it by T (Trace). It is very difficult to note differences in darkness near the zero point of the tintometer, and the errors there may easily amount to 2 or 3 degrees.

The series of tests with sucrose alone (Series I) show that practically no color was formed in any of the products by any of the different methods of clarification, no matter whether iron was added or not, and in spite of the fact that one raw juice contained as much as 12 p. p. m. of ferric iron. The more lime added to the sulfured juice, the more iron is precipitated; clarification with lime alone to slight acidity removed the iron practically completely; when it was added to slight alkalinity, a little iron remained dissolved, but was without noticeable effect on the color.

In the series of tests (Series II) where the juice contained both sucrose and reducing sugars, some color developed under certain conditions. When no iron was added to the juice there was practically no color formed as long as the juice was still acid after liming, but when lime was added to alkalinity the clarified juice showed a little color, amounting to less than one unit. In the presence of sulfites this color did not further increase upon concentration to sirup, but even decreased slightly, evidently owing to the bleaching effect of the sulfites. When lime alone was used, however, the color increased over threefold from clarified juice to sirup.

In the presence of iron the color formation was somewhat more pronounced. The clarified juices here contained considerably more iron than the raw juices, except where lime alone was added to slight acidity. The dissolved iron had practically no effect on the color in Method 1; but it produced some color where the juice in clarification was left only slightly acid, and more of it where lime had been added to alkalinity. Thus the clarified juice obtained by sulfuring and liming to slight acidity had one-half unit of color; but this did not increase appreciably on boiling to sirup, due to the protective effect of the sulfites present in solution. Where the raw juice was sulfured and limed to alkalinity, 0.9 unit of coloring matter developed, and this increased to 2.1 upon boiling to sirup. The largest amount of color was formed, as was to be expected, in the clarification with lime alone to alkalinity. The clarified juice here showed 2.6 units of color which increased to 7 units in the sirup. It is also noted that in the two cases, where the clarification was pushed to alkalinity, the sirup gave a slight reaction for polyphenols. But it must be observed that the color produced by Allen's polyphenol reaction is so slight with quantities less than 30 p. p. m. that no great reliance can be placed on the results. If the slight reaction obtained is really indicative of polyphenols, it is probably due to a decomposition of glucinic acid primarily formed, which, according to Fernand Gaud,[1] may split up into pyrocatechol and gluconic acid.

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[1] *Sucr. ind. colon.*, **44** (1894), 482.

SERIES III—SUCROSE, GLUCOSE, AND ASPARAGINE

	Acid. or Alk.	Color Red Glass	Color Green Glass	Color Blue Glass	Color, Total Degrees	Color Units	Ferric Iron	Total Iron	Polyphenols	Ferric Polyph. Compounds
					A—Without Iron					
METHOD 1										
Raw juice	1.5	0	0	1	0.1	0	..	..	..	..
Clar. juice	1.0	0	0	0	0	0	..	..	..	..
Sirup	0.9	0	0	1	0.1	0	..	..	..	..
METHOD 2										
Raw juice	1.5	0	0	1	0.1	0	..	..	..	..
Clar. juice	0.3	0	0	1	0.1	0	..	..	..	..
Sirup	0.2	0	0	1	0.1	0	..	..	..	..
METHOD 3										
Raw juice	1.5	0	0	1	0.1	0	..	..	..	..
Clar. juice	—0.3	0	1	3	1	0.2	..	..	..	..
Sirup	0	0	0	1	0.1	0	..	..	..	..
METHOD 4										
Raw juice	1.5	0	0	1	0.1	0	..	..	..	..
Clar. juice	0.3	0	0	1	0.1	0	..	..	..	..
Sirup	0.2	0	0	2	0.2	0	..	..	..	..
METHOD 5										
Raw juice	1.5	0	0	1	0.1	0	..	..	..	..
Clar. juice	—0.2	0	2	6	2	0.5	..	..	..	..
Sirup	0.1	1	10	23	9.5	3.2	..	..	..	..
					B—With Iron					
METHOD 1										
Raw juice	1.5	0	0	0	0	0	1.5	2.5	0	0
Clar. juice	0.9	0	0	3	0.3	0.1	6	9.5	0	0
Sirup	0.7	0	0	1	0.1	0	5	10.5	0	0
METHOD 2										
Raw juice	1.5	0	0	0	0	0	1	2	0	0
Clar. juice	0.3	0	0	4	0.4	0.1	9	15	0	0
Sirup	0.3	0	0	4	0.4	0.1	9	15	0	0
METHOD 3										
Raw juice	1.5	0	0	0	0	0	1.5	2.5	0	0
Clar. juice	—0.1	0	6	13	5.5	1.6	7	21	0	0
Sirup	0.1	2	13	26	12.1	4.5	7	21	0	0
METHOD 4										
Raw juice	1.5	0	0	0	0	0	1	2.5	0	0
Clar. juice	0.2	0	0	1	0.1	0	1	2	0	0
Sirup	0.2	0	0	0	0	0	2	3	0	0
METHOD 5										
Raw juice	1.5	0	0	0	0	0	2	3	0	0
Clar. juice	—0.1	3	11	21	10.4	3.7	10	21	10	11
Sirup	0.1	3	14	28	13.2	5.0	11	21	20	23

SERIES IV—SUCROSE, GLUCOSE, ASPARAGINE, AND ASPARTIC ACID

	Acid. or Alk.	Color Red Glass	Color Green Glass	Color Blue Glass	Color, Total Degrees	Color Units	Ferric Iron	Total Iron	Polyphenols	Ferric Polyph. Compounds
					A—Without Iron					
METHOD 1										
Raw juice	1.5	0	0	1	0.1	0	..	..	..	..
Clar. juice	1.0	0	0	1	0.1	0	..	..	..	..
Sirup	0.8	0	0	1	0.1	0	..	..	..	..
METHOD 2										
Raw juice	1.5	0	0	1	0.1	0	..	..	..	..
Clar. juice	0.2	0	0	0	0	0	..	..	..	..
Sirup	0.2	0	0	0	0	0	..	..	..	..
METHOD 3										
Raw juice	1.5	0	0	1	0.1	0	..	..	..	..
Clar. juice	—0.2	0	0	1	0.1	0	..	..	..	..
Sirup	0	0	0	1	0.1	0	..	..	..	..
METHOD 4										
Raw juice	1.5	0	0	1	0.1	0	..	..	..	..
Clar. juice	0.1	0	0	1	0.1	0	..	..	..	..
Sirup	0.1	0	0	1	0.1	0	..	..	..	..
METHOD 5										
Raw juice	1.5	0	0	1	0.1	0	..	..	..	..
Clar. juice	—0.1	0	1	2	0.9	0.2	..	..	..	..
Sirup	0.1	0	3	4	2.5	0.6	..	..	..	..
					B—With Iron					
METHOD 1										
Raw juice	1.5	0	0	0	0	0	1	2	0	0
Clar. juice	1.0	0	1	7	1.4	0.3	6	14	0	0
Sirup	0.8	0	0	5	0.5	0.1	6	13	0	0
METHOD 2										
Raw juice	1.5	0	0	0	0	0	2	3.5	0	0
Clar. juice	0.3	0	2	10	2.4	0.6	13	20	20	23
Sirup	0.3	0	1	8	1.5	0.3	11	21	0	0
METHOD 3										
Raw juice	1.5	0	0	0	0	0	2	4	0	0
Clar. juice	—0.2	2	4	8	4.0	1.0	7	20	0	0
Sirup	0.1	1	6	13	5.5	1.6	7	20	30	34
METHOD 4										
Raw juice	1.5	0	0	0	0	0	2	3	0	0
Clar. juice	0.2	0	2	6	2.0	0.5	5.5	9.5	30	34
Sirup	0.2	0	2	12	2.6	0.6	7	15	50	56
METHOD 5										
Raw juice	1.5	0	0	0	0	0	1	2	0	0
Clar. juice	—0.2	2	7	17	6.8	2.0	8	20	20	23
Sirup	0.1	12	23	34	22.0	9.1	8	20	60	67

Glucinic acid itself gives an iron reaction, but not Allen's reaction. The iron reaction is probably due to its nature as a polyoxy-acid, and it may be intensified by pyrocatechol formed secondarily.

We shall now pass on to Series III, in which asparagine, and Series IV, where asparagine and aspartic acid were added to sucrose and reducing sugars in preparing the raw juice. It has been shown by Maillard,[1] by Lafar,[2] and by Oudemans,[3] that nitrogenous coloring matters are formed by the effect of amino acids and their derivatives on reducing sugars, and that the products obtained in the presence of alkali are even more highly colored than those made in acid solution. Since cane always contains a small quantity of acid amides, principally asparagine, and of amino acids, probably mostly aspartic acid, in addition to which small amounts of other cleavage products of proteids are formed during clarification, it was necessary to extend our work to tests made in the presence of these compounds. But the results of Series III and IV show that the effect of the very limited quantity of these substances found in cane juice is not so very great. As long as the juice, after the lime treatment, is still acid, the color developed is in no case much greater in the presence of asparagine, or of a mixture of asparagine and aspartic acid, than in their absence. Where iron chloride was not added the color formed in the first four methods of clarification was about the same as in Series II, and in Method 5 even slightly less. In the presence of iron, Clarification Methods 1, 2, and 4—that is, those with final acidity—produced only about as much color as where the nitrogenous compounds were left out, with only a little more color where both asparagine and aspartic acid were added. In Clarification Method 3, the products with asparagine gave only a slightly darker clarified juice and sirup than without asparagine; in Method 5 the clarified juice was somewhat darker, but the sirup somewhat lighter than in the corresponding method in Series II. Where both asparagine and aspartic acid were employed, the clarified juice obtained by sulfuring and liming to slight alkalinity was about the same color as without the nitrogenous compounds, and the sirup was even a shade lighter. Conversely, in the clarification with lime alone to slight alkalinity the clarified juice was a little lighter, but the sirup quite a bit darker.

Taking it all in all, the very small quantities of amino acids and their derivatives do not seem to exert very much influence on the color of the products. It is noteworthy, however, that in the sirup obtained by Method 5 in Series III a slight reaction for polyphenols was again obtained, and that such positive reactions were even more numerous in Series IV. These findings are quite in accord with the results of Maillard,[1] and of Stoltzenberg,[2] who showed that the nitrogenous coloring matters formed from amino acids and reducing sugars have a cyclic structure, and contain hydroxyl groups. Here we evidently have to do with true polyphenols, but their iron compounds are not as dark as those with tannin, as will become apparent when the results of Series IV are compared with those of Series V.

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[1] *Compt. rend.*, **156** (1912), 66.

[2] *Intern. Sugar J.*, **16** (1914), 184, 230.

[3] *Arch. Suikerind.*, **26** (1918), 1686.

[1] *Loc. cit.*

[2] *Ber.*, **49** (1916), 2021.

SERIES V—SUCROSE, GLUCOSE, ASPARAGINE, ASPARTIC ACID, AND TANNIN

	Acid. or Alk.	Color Red Glass	Color Green Glass	Color Blue Glass	Color. Total Degrees	Color Units	Ferric Iron	Total Iron	Polyphenols	Ferric Polyph. Compounds
					A—Without Iron					
METHOD 1										
Raw juice	1.5	2	4	7	3.9	1.0	0	0.5	170	0
Clar. juice	0.9	17	16	19	15.5	6.2	0	0.5	100	0
Sirup	0.8	14	17	17	16.4	6.7	0	0.5	100	0
METHOD 2										
Raw juice	1.5	1	2	6	2.2	0.5	0	0.5	170	0
Clar. juice	0.3	6	12	16	11.2	4.1	0	0.5	90	0
Sirup	0.3	6	15	21	13.8	5.4	0	0.5	80	0
METHOD 3										
Raw juice	1.5	1	3	6	2.9	0.7	0	0.5	170	0
Clar. juice	—0.1	1	11	24	10.3	3.7	0	0	80	0
Sirup	0	5	15	27	14.2	5.6	0	0	70	0
METHOD 4										
Raw juice	1.5	1	3	5	2.8	0.7	0	0.5	190	0
Clar. juice	0.3	30	35	45	35.0	15.8	0	0.5	180	0
Sirup	0.3	30	35	44	34.9	15.8	0	0.5	170	0
METHOD 5										
Raw juice	1.5	1	3	7	3	0.7	0	0.5	190	0
Clar. juice	—0.2	28	27	43	28.8	12.5	0	0.5	120	0
Sirup	0.2	25	30	45	30.5	13.4	0	0.5	140	0
					B—With Iron					
METHOD 1										
Raw juice	1.5	18	17	24	17.9	7.3	6	14	170	48
Clar. juice	0.9	42	40	38	40.0	19.2	4	13	50	32
Sirup	0.7	38	39	39	38.8	18.4	5.5	14.5	70	44
METHOD 2										
Raw juice	1.5	16	18	22	18	7.3	5.5	13.5	170	44
Clar. juice	0.3	40	43	46	42.7	21.3	3.5	13.5	70	28
Sirup	0.3	38	44	45	42.9	21.4	6.5	16.5	70	52
METHOD 3										
Raw juice	1.5	18	17	22	17.7	7.2	5.5	13.5	170	44
Clar. juice	— 0.1	30	46	52	43.4	22.0	6	18	60	48
Sirup	0.2	33	47	50	44.5	22.8	6	18	60	48
METHOD 4										
Raw juice	1.5	16	18	21	17.9	7.3	5	13	170	40
Clar. juice	0.3	58	57	58	57.3	34.3	8	18	100	64
Sirup	0.3	57	59	59	58.6	35.6	8	18	120	64
METHOD 5										
Raw juice	1.5	18	18	20	18.2	7.4	7	16	170	56
Clar. juice	—0.1	40	59	66	55.9	33.1	7	19	70	56
Sirup	0.1	41	59	64	55.9	33.1	6	18	70	48

The results obtained so far show that a juice containing sucrose, glucose, potassium asparaginate, potassium aspartate, and aconitic acid will, upon clarification and boiling to sirup, develop any considerable color only when lime is added to alkalinity; in the presence of iron the color produced is roughly two to three times as much. If sulfur is used, in addition to lime, the color is considerably less, owing to the bleaching action of sulfurous acid, and even of sulfites in solution or suspension. And most important of all, in the method of clarification generally used in white sugar manufacture in Louisiana, where the juice is strongly sulfured and limed back to decided litmus acidity, any decomposition products of glucose formed, even in the presence of amino acids, amides, and iron, do not produce any considerable color, under normal working conditions, that is, when the products are not heated too high and too long. The large amount of coloring matter which we actually do find in the clarified juice and sirup made by this process in the factory must therefore be almost entirely due to other causes than to decomposition products formed from reducing sugars.

As we had already found in our sugar-house tests that the polyphenols occurring in the cane, or formed in the process of manufacture from other substances present in the cane, like saccharetin and anthocyanin, evidently form a considerable proportion of the coloring matter, we added, in Series V of our experiments, to the constituents used in Series I to IV, a small quantity of the iron-greening tannin isolated by us from the cane. The addition of this substance produced a remarkable effect on the color of all our products, as may be seen by a mere glance at Series VI.

SERIES VI—TOTAL COLOR OF PRODUCTS

	Sucrose	Sucrose Glucose	Sucrose Glucose Asparagine	Sucrose Glucose Asparagine Asp. Acid	Sucrose Glucose Asparagine Asp. Acid Tannin
		A—Without Iron			
S, L, 1.0 Cc. ACID					
Raw juice	T	T	T	T	1.0
Clar. juice	T	T	T	T	6.2
Sirup	T	T	T	T	6.7
S, L, 0.3 Cc. ACID					
Raw juice	T	T	T	T	0.5
Clar. juice	T	T	T	T	4.1
Sirup	T	T	T	T	5.4
S, L, 0.3 Cc. ALK.					
Raw juice	T	T	T	T	0.7
Clar. juice	T	0.8	T	T	3.7
Sirup	T	0.7	T	T	5.6
L, 0.3 Cc. ACID					
Raw juice	T	T	T	T	0.7
Clar. juice	T	T	T	T	15.8
Sirup	T	T	T	T	15.8
L, 0.3 Cc. ALK.					
Raw juice	T	T	T	T	0.7
Clar. juice	T	0.9	0.5	T	12.5
Sirup	T	3.1	3.2	0.6	13.4
		B—With Iron			
S, L, 1.0 Cc. ACID					
Raw juice	T	T	T	T	7.3
Clar. juice	T	T	T	T	19.2
Sirup	T	T	T	T	18.4
S, L, 0.3 Cc. ACID					
Raw juice	T	T	T	T	7.3
Clar. juice	T	0.5	T	0.6	21.3
Sirup	T	0.6	T	T	21.4
S, L, 0.3 Cc. ALK.					
Raw juice	T	T	T	T	7.2
Clar. juice	T	0.9	1.6	1.0	22.0
Sirup	T	2.1	4.5	1.6	22.8
L, 0.3 Cc. ACID					
Raw juice	T	T	T	T	7.3
Clar. juice	T	T	T	0.5	34.3
Sirup	T	T	T	0.6	35.6
L, 0.3 Cc ALK.					
Raw juice	T	T	T	T	7.4
Clar. juice	T	2.6	3.7	2.0	33.1
Sirup	T	7.0	5.0	9.1	33.1

Taking first the raw juices made without iron, we find quite a perceptible amount of color, even though there can be only mere traces of iron present. The color is mostly due to a slight oxidation of the tannin, taking place soon after it is dissolved. As we have seen before, the color of an actual cane raw juice of the same composition would be much darker, even in the absence of iron, on account of the effect of the oxidases in the juice.

Passing now to the clarified juices in the absence of iron, we make the important observation that the clarification methods themselves bring about formation of coloring matter from the tannin, although a part of the latter is removed. Of the methods with sulfur and lime, Method 3 took out the largest quantity of tannin, and the clarified juice here had only 3.7 color units; Method 2 removed less tannin, and a little more color was found; Method 1 removed the least, and the color was darkest. However, from clarified juice to sirup, the increase in color is least in Method 1, and most in Method 3, probably owing to the more effective bleaching effect of sulfites at higher acidity. The final result is that the sirups obtained by Methods 2 and 3 have about the same color, 5.4 and 5.6 units, respectively, and that from Method 1 slightly more, 6.7. In the two methods of clarification without sulfur, the color is much darker than in the others, once more proving the bleaching effect of the sulfites and sulfurous acid. Here again the larger amount of lime removed more tannin than the smaller amount, and for this reason the clarified juice in Method 5 is lighter than in Method 4, in spite of the fact that in this case the decomposition products of glucose should give rise to a darker color, as was found in Series II, III, and IV. From clarified juice to sirup there was found no increase in color in Method 4, and only a slight one in Method 5. It seems as if the excess of alkali acted first on the tannin, before affecting any of the reducing sugars.

We now turn to the most important tests of the series, in which the products most closely approach the ones obtained from the cane. Another glance at Series VI shows that the cane tannin in connection with iron actually gives rise to very dark-colored products. In the raw juices we find that a ferric iron content of 5 to 7 p. p. m. produces, in the presence of an excess of tannin, a color of 7.2 to 7.4 units. This is admittedly considerably less color than we found in raw juices having approximately the same composition; and more than that, the tint of the juices was different, those from the cane showing for the same amount of green much more red and yellow. This is no doubt due to the presence in cane juice of the yellow and red coloring matters of the rind, plus the brown oxidation products of the tannin. Thus a comparison of the natural juices with the artificial ones with tannin as the only polyphenol shows that the tannin as such is only partially responsible for the color of raw cane juice.

In clarification, the juices with iron behave somewhat differently from those without it. While it is true that all the clarified juices are again much darker than the raw juices, the color of the former does not decrease from Method 1 to Method 3, but slightly increases. This is evidently due not so much to an increase in iron polyphenol compounds, because the ferric iron in clarified juice of Method 2 is slightly lower than in that made by Method 1; the most important reason probably lies in the well-known fact that the color of the iron polyphenol compounds increases with decreasing acidity. But it is interesting to note that the clarified juice in Method 2 is not nearly as much darker than that in Method 1 as we would expect from parallel tests in the sugar house, where Method 1 gave an increase in color from 16.5 and 13, in raw juice, to 26 and 22.5, respectively, in clarified juice, and Method 2 one from 12.5 to as high as 32, even though in the latter case the iron polyphenol compounds were lower than in the first two. This again points to the presence of other cane juice constituents contributing to the formation of coloring matter, besides the iron-greening tannin.

Clarification with lime alone produced much darker juices than that with sulfur and lime, owing to the absence of the bleaching effect of the sulfites. Liming to alkalinity did not produce a darker juice than liming to slight acidity, evidently due to the fact that the effect of the smaller quantity of iron polyphenol compounds in Method 5 overbalances the darkening otherwise produced by the lower acidity. Series V further shows that those methods in which lime is not added to alkalinity produce clarified juices of about the same tint as the raw juices, only much darker; but where lime is added to alkalinity, the clarified juices show more red and yellow.

Between the clarified juices, on the one hand, and the corresponding sirups on the other, there is very little difference in color. This shows once more that the decomposition products of glucose by heat, even in the presence of excess alkali and of amino acids have no great effect on the color of at least the clarified juice and the sirup. The sirups again show a larger proportion of red and yellow where lime was added to alkalinity.

CONCLUSIONS

The following conclusions may be drawn from all the results. In clarified juices and sirups made under normal conditions by the methods of clarification generally practiced in Louisiana, very little color is due to decomposition products of glucose by heat in the presence of amides and amino acids, and even where lime is added to slight alkalinity in clarification, their effect on the color is still slight. The iron-greening tannin of the cane, however, evidently has a pronounced effect in producing color, especially in the presence of ferric salts. But the tannin mentioned is not alone responsible for the color of the clarified juices and sirups. The oxidation products of this tannin by oxidases as well as the anthocyanins of the rind, and the saccharetin of the fiber evidently also play an important part. It has been mentioned above that red canes give darker products than light-colored ones, and that juices from which the finely divided fiber or bagacillo has been but imperfectly removed likewise give rise to inferior products. Both anthocyanins and saccharetin belonging to the polyphenols, it appears very probable that the pronounced increase in color occurring in the factory between clarified juice and sirup, and which we did not find to occur in our artificial juices containing only the constituents used so far by us, is due to the substances mentioned above. Our further investigations are expected to throw more light on this subject.

Some very important practical deductions may be drawn from the results obtained so far. Our factory experiments of last year, and again the tests reported in this paper, have clearly demonstrated that in the presence of polyphenol compounds and their derivatives, and at the same time of iron salts, the chemical methods of juice purification practiced in Louisiana, even sulfitation with high final acidity, produce clarified juices which are not lighter but often even appreciably darker than the raw juices from which they are obtained. It follows that from the standpoint of the manufacture of high-grade products, as explained in the introduction to this article, our methods of purification do not bring about an improvement, but rather a decrease in the quality of the juice, and do not effect what, according to Prinsen-Geerligs, is the principal object of clarification; namely, the removal of coloring matter and other colloidal impurites. It is becoming more and more clear that the solution of the problem will have to be sought along the lines of colloid chemistry, as pointed out by Peck[1] and by others. It is true that the precipitates produced by the chemical methods now in vogue in Louisiana tend to carry down some of the coarser dispersoids of cane juice, but they are very inefficient in this respect.

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[1] *Intern. Sugar J.*, **21** (1919), 70.

This brings us then to the question of removing not only coarse dispersoids, but colloids as well. It seems certain that what is done so imperfectly now by the precipitates produced through the addition of chemicals to the juices can probably be accomplished much better by physical adsorption. It is known that certain forms of carbon, especially the so-called decolorizing carbons, are under certain conditions very effective in removing colloids. There may be yet other ways, based on principles of colloid chemistry, which might lead to success. The feasibility of the use of decolorizing carbons for the purpose in hand has already been amply demonstrated, but the economical side of the problem still remains to be worked out in detail.

SUMMARY

It has been found by a study of artificial juices, resembling cane juice, that in the methods of clarification generally practiced in Louisiana the dark color actually found in our factory products appears to be almost entirely due to several polyphenol derivatives occurring in cane juice. When ferric salts are also present, as is always the case in the factory, the color is two to three times as dark as with the polyphenols alone. The iron-greening tannin isolated by us from cane juice is not alone responsible for the color, but other polyphenol derivatives, *viz.*, anthocyanin and the saccharetin of the cane fiber, also seem to play an important part. Further researches on the effect of these latter two constituents are contemplated.

It has been shown again, as had been found in previous sugar-house experiments, that the methods of clarification at present employed in Louisiana do not effectively remove these colloidal substances, and that the clarified juices are darker than the raw juices from which they were obtained. The solution of the problem of cane-juice purification must evidently be sought in the field of colloid chemistry.

THE PRESERVATION OF EGGS, INCLUDING A BIBLIOGRAPHY OF THE SUBJECT

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Egg dealers handling millions of eggs a year report losses from spoilage as high as 25 per cent. It is surprising, in view of the time that has been spent upon the problem of preservation of eggs, to note the small number of methods developed. The United States, France, and Germany have done the most work upon egg preservation. Comparatively little research seems to have been done in England.

Perhaps the earliest expedient was to bury or pack eggs in an airtight substance. More recently the substitution of some inert gas has accomplished the same purpose. Calvert (France)[1] in 1873 kept eggs, either whole or pierced, in N_2, H_2, or CO_2 for 3 mo. When kept in dry oxygen the eggs suffered no change, provided the samples were infertile, but in moist oxygen a white mold was formed. The ideal condition of absolute dryness never exists in practice. Fernand Lescarde[2] in 1909 used carbon dioxide as the preservative medium, but modified the procedure to include sterilization of the egg. Eggs were subjected to reduced pressure to remove the air and then impregnated with carbon dioxide under pressure in order to kill the bacteria within the shell. They were then placed in an atmosphere of carbon dioxide (94 per cent) and nitrogen (6 per cent) and kept at nearly 0° C.

The shell of an egg is very porous. If it were not most eggs would not spoil. The germ could not grow without a supply of oxygen, and external contamination could not take place. Upon this fact most preserving processes depend for their efficacy.

There are two main elements in the problem of preservation, *viz.*, sterilization, and defertilization. The loss of eggs is due to the catabolic activity of bacteria present in the egg and to the growth of the living germ with the consequent destruction of the substance and properties of the egg. Defertilization means either the immediate destruction of the germinal vesicle, or its inhibition and final destruction through lack of air.

The use of inert gases for asphyxiation of the embryo is impracticable, and would not stop evaporation. Keeping eggs in a vacuum would deprive the germ of oxygen, but it is difficult to maintain a vacuum for any length of time and it would greatly hasten evaporation. The majority of preservative processes have depended for their effect on the simple exclusion of air by some sealing agent.

METHODS OF PRESERVATION

All of the methods can be grouped in four classes according to whether the eggs are preserved: (1) At low temperatures without preliminary treatment, (2) by packing in comparatively airtight substances, (3) in the dry state after coating with various impervious agents, or (4) in solutions with or without preliminary treatment.

(1) At the present time storage at low temperatures is most relied upon, when the eggs are not to be transported. The temperature of the storage rooms is maintained just above the freezing point of the egg. This is 0.4270° to 0.4800° C. at first and rises slightly during incubation, corresponding to a rise of osmotic pressure from 5.5 to 7.3 atmospheres.

Cold storage can be successfully used only when the surrounding atmosphere is dry and the eggs are kept dry. Calvert[3] showed that the least moisture will cause the formation of shell mold and hasten putrefaction. Even in dry surroundings the temperature of storage is not sufficient to kill the germinal cell. Growth is merely inhibited until the eggs are released for shipment. Spoiling is then accelerated because the long subjection to cold has broken down the white and destroyed the germicidal power which the egg possessed when fresh.

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[1] *Compt. rend.*, **67** (1873), 1024.

[2] *Ber., II Intern. Kaltekong., Wien*, **2** (1910).

[3] *Loc. cit.*

(2) Packing in various materials is an old and much used preservative process. Salt, bran, sand, lime, sawdust, ashes, and sulfur are commonly used. Most of these processes have not been successful. The looser packings allow evaporation and the growth of mold, while others merely inhibit the growth of the germ. The main objection against these preservatives is the slowness of the processes and the necessity of transporting the packing materials with the eggs.

(3) Methods which consist in coating the egg with an impervious and sometimes antiseptic substance are free from this latter objection. If eggs could simply be dipped and stored without further treatment, the process might be successful, but many processes of coating require that the eggs be individually smeared with the material, and in commercial competition cannot hope for success.

(4) No preservative solution, however effective it may be, can compete commercially with preservative coating. The necessity of keeping the eggs immersed in the liquid makes shipment burdensome and expensive. The weight of the containers themselves is a large item in the cost of transportation. For home use solutions are perhaps most convenient, requiring little care in application or packing, and easily made on the spot or else readily purchasable.

The consensus of opinion indicates that no solution has yet been found which is superior to water glass. Its solution is highly viscous, involatile, and a poor solvent of gases. The high viscosity and the slight occlusion of gases explain its success in keeping air away from eggs. The concentration generally used is a 10 per cent solution. The eggs must not be stale or contaminated, as this method does not sterilize or inhibit bacterial growth. The eggs must be kept immersed by a weight and cannot be kept out of the solution more than a few weeks. Hendrick[1] gives some tables showing that no change took place in eggs kept in water glass for 4 yrs. In the third or fourth year the white became pink and tasted of soda.

COMPARISON OF SEALING AGENTS

In order to record the relative efficacy of sealing agents the water-glass coefficient was developed. Eggs were treated with various sealers and placed in an incubator at 37.5°. The materials compared were a gasoline solution of aluminum soap, a gasoline solution of paraffin, a water-glass solution, vaseline, and egg white. At the end of 2 wks. the aluminum-soap eggs were in perfect condition, the water-glass eggs were not good, and the rest were completely spoiled.

To have found the absolute value of the various treatments, *i. e.*, the actual time of keeping, would have required several years. Hence all our results are relative, and for relative results no absolute standards of measurements are necessary. Fresh fertile eggs were found to keep at laboratory temperature (20° C.) for as long as a month without more than a slight enlargement of the germinal cell. Water glass will keep them for at least 2 yrs., often 4. Incubation simply shortens the time required for the changes to take place, without modifying them. Eggs treated in various ways and incubated were compared with eggs immersed in water glass and kept at the same temperature. This comparison afforded a means of translating all relative results into absolute figures. The water-glass coefficient can be obtained just as the phenol coefficient for disinfectants, by finding the number of days in the incubator required for spoiling water-glass eggs, and affords a ready means of finding the absolute efficacy of any preservative. It was found that eggs in water glass at 37.5° C. spoiled in 4 wks. Eggs kept in aluminum soap were perfectly fresh at the end of that time. Most preservatives have a water-glass coefficient less than one, a very few—preëminently aluminum soap—greater than one. Unless the coefficient is greater than two, it can be determined in 4 to 8 wks. The average preservative power of water glass expressed in days multiplied by the coefficient will give the time of preservation by the method in question.

The chief cause of the failure of such sealing agents as paraffin and shellac is that they crack upon cooling and drying. The failure of sealing by simple immersion in the case of these substances indicated the necessity of impregnating the eggs with sealing agents. Impregnation by difference of pressures was used. The eggs were placed in the sealing solution and the pressure was reduced to about 20 mm. As soon as the evacuation of the egg is complete, shown by no more air bubbles rising, the normal pressure is suddenly restored. This, of course, caused the sealer to be forced into the pores of the shell. At the end of 4 wks.' incubation the method was shown to have produced better sealing. The eggs thus treated with paraffin and with water glass were not good, but were in much better condition than in the first test. Those sealed under pressure with aluminum soap were as fresh as ever.

ALUMINUM SOAP

The superiority of aluminum soap over other sealers, indicated by the previous test, seemed to justify its selection for special experiment to determine the necessary conditions for its success, its shortcomings of whatever nature, and the remedies for them.

Aluminum soap can be prepared from any kind of soap, but for our purpose the cheapest soap was selected. It is an odorless, tasteless solid, and makes an ideal sealer since it is without effect on the egg. But the necessity of providing some solvent complicates the problem. The necessary requirements of a solvent for the soap are: (1) That it shall dissolve the sealer easily at low temperature, (2) that it shall be volatile, and (3) that it shall be without effect upon the egg. Of the many solvents tried gasoline was selected as the only liquid worthy of consideration.

In this work the time required for a single incubation made it advisable to run as many different sets of eggs as possible at the same time, using the same controls for all. This practice afforded a cross-comparison of results. Eggs were treated with aluminum soap with various modifications in order to determine how the sealing should be done to effect maximum preservation.

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[1] Aberdeen and Nova Scotia College of Agriculture, *Bulletin* **8**; also *J. Agr. Sci.*, [1] **2** (1907).

Impregnation under pressure was tried, as it was considered possible that subjection to a vacuum for a long time might affect the germinal cell. Our eggs were all fertile, and, after incubation, afforded striking demonstrations of the effect of different treatments. Two days' incubation showed that with aluminum soap impregnation under pressure is not necessary to the best preservation. Dipping in dilute sulfuric acid has seemed to produce better results, and for the best results under the most rigorous conditions this should be the initial treatment. In every case old eggs kept as well as fresh ones. The good results achieved with them show that our method of preservation is successful with the ordinary market eggs, which fact constitutes a point of superiority over most processes.

Eggs immersed in the aluminum soap were exposed to a very low pressure maintained for an hour. This long evacuation practically sterilizes the egg. When atmospheric pressure is suddenly restored the tendency of the air to rush into the egg causes the soap solution to impregnate the pores. The eggs are then drained and stored or packed for shipment. As the gasoline evaporates an airtight, waterproof, elastic coating is left on the eggs, which prevents access of air. Sterilization is followed by defertilization. As a practical process of sterilization at this time, however, long-continued exhaustion is not wholly successful, and much work remains to be done.

The great shortcoming which a gasoline solution of aluminum soap has is that a slight taste of gasoline is left in the egg. This process of preservation must be made tasteless or it cannot be used. Two methods of solving the problem were tried and both were successful. The first was to protect the eggs by a preliminary coating before sealing with the gasoline solution. The best agent for this purpose is dilute sulfuric acid. When eggs are immersed in the acid effervescence continues for about 10 sec. and ceases as a coating of calcium sulfate is formed in the pores of the eggs. The calcium sulfate acts as a polarizer and stops the reaction. The eggs are then dipped, without drying, into the aluminum soap solution and placed on a special dripping rack. The method of double sealing with sulfuric acid seems wholly satisfactory. The contents of the egg is sweet; no taste of gasoline can be detected. The extra cost of the preliminary sealing, either in time or money, is negligible.

The necessity of double dipping is without doubt a weakness, and a better solution of the problem was found. First, an attempt was made to purify gasoline. The taste and smell of commercial gasoline are due to minor constituents, chiefly unsaturated olefines, free sulfur, mercaptan compounds and other substances. Agitation for several hours with concentrated sulfuric acid, reduction for 3 days with Gatterman copper, distillation over copper oxide, and filtration through animal charcoal failed to eliminate entirely the odor and the taste of gasoline.

Gasoline is largely composed of pentane, a practically tasteless, odorless, and colorless liquid, boiling at 37°. Since gasoline dissolves aluminum soap well, it was certain that its chief constituent would do so, and the problem was to prepare chemically pure pentane on a large scale.

The best method of preparing pentane seems to be the reduction of amylene. A very convenient and cheap process for making amylene or pentane has recently been devised by Roger Adams.[1] The amylene vapors thus produced by Adams' pyrogenic catalytic method are passed without further purification through a heated tube (300°) containing pyrophoric nickel in the presence of hydrogen. By fractional distillation practically odorless and tasteless pentane can be produced.

By this process, the 125° to 130° fraction from technical fusel oil may be introduced a liter at a time and supplied to the generator indefinitely without exhaustion of the catalyst. The cheapness with which pentane may now be made and the facility with which the product can be used to dissolve aluminum soap seem to make this solution of the problem satisfactory in every way.

VACUUM TREATMENT

Vacuum treatment without aluminum soap did not in any case entirely preserve the eggs, but it did afford a test of the effect of varying amounts of evacuation on the growth of the germ. Out of four sets subjected to evacuation, three showed that this had an effect in repressing germinal growth. A gradual increase in the quality of the eggs was seen corresponding to a longer exposure to vacuum. Evacuation thus seems to be a powerfully contributing factor in the preservation of eggs, being able by itself to inhibit, if not entirely to prevent, the growth of the germ.

The question of the permeability of eggs to bacteria has received much attention and researches have definitely proved that bacteria do enter from the outside. Bacteria do not easily infect a dry egg, because of the natural mucilaginous coating which hardens and prevents for a short time evaporation and contamination. However, undue handling and the too frequent practice of washing soon deprive the egg of this protection. The porosity of the shell as evidenced by the respiration of the growing germ always guarantees the presence of oxygen in the egg, making impossible the growth of all non-sporulating and obligatory anaërobes since such bacteria require absolute absence of oxygen. There is also little probability of non-motile organisms penetrating the shell.

Tests were run to determine the number of bacteria in fresh eggs. Whole eggs were carefully transferred to Petri dishes, whites alone, and yolks alone. They were incubated at 37.5° for 48 hrs. In this time only one colony developed in eight eggs and a slight amount of gas was formed in one dish. The cause of the spoiling of eggs, then, is not in general congenital bacteria but those acquired from infected materials. Old nesting material, unclean hands, careless packing in any kind of receptacles, and storage in dirty containers produce an accumulating contamination. For this reason eggs on the market are almost sure to spoil if kept long enough at moderate temperatures. The presence of a bacterial flora whose density increases with age contributes the worst element in the problem of preservation, namely, sterilization. The sterilization of an egg is most difficult. Strictly anaërobic organisms cannot live in an ordinary egg. Of the bacteria that may be present at the time of preservation all are almost necessarily aërobes, but some may become facultatively anaërobic under anaërobic conditions. Our process reduces to a small number the bacteria which may survive and cause putrefaction. The normal bactericidal power of ordinary eggs may destroy these.

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[1] University of Illinois, *Bulletin* 16, No. 43, 13.

The possibility of destroying bacteria by use of a vacuum is a question of immediate practical bearing here, and also of great theoretical interest in bacteriology. Prof. B. H. Hite of the University of West Virginia has succeeded in destroying bacteria by subjecting them to high pressures. Almost any organism is more resistant to high than to low pressure and to a sudden raising of the pressure than to a sudden lowering. That any organism could rapidly and completely adjust itself to a sudden reduction of pressure was considered on theoretical grounds to be impossible. Successful results in demonstrating this hypothesis were expected to be valuable in the sterilization of any limpid liquid. Viscous liquids do not permit the evacuation to extend quickly enough to all their parts. An extended experiment was projected to determine the effect of evacuation, both sudden and gradual, on bacterial cultures in liquid media. Sudden evacuation would not be applicable to eggs, but the success or failure of the most extreme method of exhaustion would indicate the success to be expected from gradual treatment.

The quickest and most effective way of producing a vacuum was to connect a small sealed container at atmospheric pressure to a much larger cylinder which was highly evacuated; the resulting equalization of pressures producing a low final pressure almost instantly. The cylinder we used had a capacity of 279.08 liters, and the bottle containing the eggs had a capacity of 700 cc. The volume ratio was 1 : 398.9. With atmospheric pressure and absolute vacuum the resulting pressures from this ratio would be 1.85 mm. of mercury. Our cylinder vacuum was from 1 to 4 mm. Our results showed that this arrangement may produce great bactericidal effects, but seemed never able to sterilize the eggs entirely. We are continuing this phase of the work.

Tests of the effect of ultraviolet light were made and it was shown to have no destructive effect either on the bacteria or germ in the egg. At the end of four days' treatment the results indicated that a combination of ultraviolet light and evacuation treatments had reduced the growth. In all cases the amount of growth was less than that produced by the controls, but ultraviolet light alone was without bactericidal effect in the case of eggs.

Our anticipatory opinion that sudden evacuation would have a germicidal power and that it would be more effective than gradually produced and long-continued exhaustion was corroborated by the results of our experiments. Though a sudden evacuation cannot be applied to the sterilization of eggs, these results are not valueless for they indicate that even long-continued evacuation may sometimes be used successfully for sterilizing eggs, if the pressure be reduced sufficiently. If this method of sterilization can be made effective our process of preserving eggs will become complete.

SUMMARY

I—Methods of preservation of eggs are grouped in four classes: (*a*) low temperature storage, (*b*) airtight packing, (*c*) sealing with various agents, and (*d*) immersing in preservative solutions.

II—A water-glass coefficient was developed by which the efficacy of sealing agents might be determined.

III—Comparison of sealing agents showed the superiority of aluminum soap.

IV—It was necessary to find a suitable solvent for the aluminum soap:

(1) When gasoline was used, a preliminary coating with dilute sulfuric acid prevented any taste from the gasoline being left in the egg.

(2) Chemically pure pentane, a constituent of gasoline, makes an ideal solvent, and a commercial method of its preparation was developed.

V—Vacuum treatment without the use of a preservative showed a bactericidal effect, but did not entirely preserve the egg.

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A VOLUMETRIC METHOD FOR THE DETECTION AND ESTIMATION OF NEUTRALIZERS IN BUTTER AND IN CERTAIN ALLIED PRODUCTS[1]

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In the manufacture of butter from cream too acid for making an acceptable product, it is the practice to add some neutralizing agent, such as lime or soda ash. Normally, the alkaline salts[2] occurring in fresh milk are the dibasic phosphates and the citrates of calcium, potassium, sodium, and magnesium, and the calcium that is combined with the proteins. When milk sours under ordinary conditions the lactic acid formed reacts[3] with these basic constituents to form acid phosphates, citrates and lactates, and free casein. Since citrates are gradually fermented[4] in souring milk to produce a certain amount of acetic acid, which, together with lactic acid, may be extracted with ether, it is sufficient to consider here only the phosphates and lactates.

The reaction in which the dibasic phosphates are changed to monobasic salts being reversible, as shown in the following equation, it is evident that in sour cream

$$2CaHPO_4 + 2H.C_3H_5O_3 \rightleftarrows Ca(C_3H_5O_3)_2 + CaH_4P_2O_8$$

there exists a condition of salts which would be changed if all or a portion of the free lactic acid were neutralized. Since it is impractical to remove all the salts of milk from butter, it follows that the condition of the milk salts in butter from neutralized cream will differ from that of the salts of butter from normal cream.

By the procedure described in this paper for the detection of neutralizers, all of these salts are separated from the milk proteins by treating the sample with a known amount of 0.1 *N* hydrochloric acid and an excess of picric acid, filtering and extracting the lactic acid and the excess of picric acid with ether. On titrating the remaining solution with sodium hydroxide, using methyl orange or a similar indicator, butter yellow, for instance, the excess of the hydrochloric acid added over the amount neutralized by the sodium hydroxide will be the alkalinity of the salts or the amount that has combined with the bases formerly present as alkalies, lactates, and phosphates, as shown by the following equations:

$$\underset{\text{Calcium lactate}}{Ca(C_3H_5O_3)_2} + 2HCl = CaCl_2 + \underset{\text{Lactic acid}}{2HC_3H_5O_3} \qquad (1)$$

$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2 \qquad (2)$$

$$CaHPO_4 + 2HCl = CaCl_2 + H_3PO_4 \qquad (3)$$

$$H_3PO_4 + NaOH = NaH_2PO_4 + H_2O \qquad (4)$$

In the above procedure it is evident that the greater the amount of neutralizer added the greater will be the amount of hydrochloric acid used, whether the alkali still exists as such or has neutralized the lactic acid to form a lactate.

In normal milk and milk products the alkalinity of the salts contained in them has been found to bear a definite ratio to the inorganic phosphoric acid, being about 45 cc. of normal solution per gram of phosphoric acid. In a neutralized milk this ratio will be increased to a degree dependent on the amount of alkali added and the per cent of phosphoric acid in the sample. The butter made from a neutralized cream then would have an alkalinity ratio similar to that of the cream from which it was made, if all the salts were removed in the same proportion during the manufacture. Results obtained indicate that this is generally the case if cream when churned contains enough free lactic acid to hold the phosphate in solution. However, if all the acid is neutralized and the cream then churned, the butter made from it may have a lower alkalinity ratio than the neutralized cream.

PROCEDURE FOR DETERMINING ALKALINITY

FOR BUTTER—Melt about one pound of butter in a closed Mason jar at 45° and cool, shaking almost constantly until the butter is about the consistency of thick cream. Determine the water in the sample by the A. O. A. C. method. Weigh 100 g. of the butter into a wide-mouthed, ground-glass stoppered bottle of 250 cc. capacity, add gasoline warmed 5° or 10° above room temperature, stopper the bottle tightly, and shake well until the butter fat dissolves. Centrifuge and syphon the fat solution, using very gentle suction to draw off the last portion. To the residue add 50 cc. of 0.1 *N* HCl and 100 cc. of a saturated solution of picric acid, stopper tightly, and shake constantly for one-half hour, or at intervals for 2 hrs. Cool and filter on a dry paper. Extract a 50 cc. aliquot of the filtrate with ethyl ether in a liquid extracting apparatus for 20 hrs., when the solution should be colorless. Transfer to a 200 cc. Erlenmeyer flask and boil gently, until all carbon dioxide is expelled. The tube (Fig. 1) should fit into the flask so that a seal is formed at A by the condensed vapors. The constrictions at B and C should be about 7 mm. in internal diameter, so that the steam will be well washed by the backflowing condensed liquid and yet without danger of mechanical loss by spattering. Cool and titrate with 0.1 *N* NaOH, using either methyl orange or butter yellow, preferably the latter since it gives a more distinct color change. Calculate the 0.1 *N* HCl in the aliquot, taking as the total volume of the solution 150 cc. plus the water in the sample. This result minus the 0.1 *N* NaOH used in the titration will give the alkalinity of the aliquot. Take a smaller sample of butter, if the alkalinity of the aliquot is more than 7 cc. This will be necessary, however, only when the butter contains an unusually large amount of buttermilk. Add 10 cc. of magnesia mixture, 10 cc. of concentrated ammonia and let the solution stand over night. Filter and wash twice with ammonium hydroxide containing 2.5 per cent of ammonia and dissolve the precipitate in hot, dilute nitric acid. Determine P_2O_5 in the solution by the A. O. A. C. volumetric method. The alkalinity as 0.1 *N* cc. divided by the milligrams of P_2O_5 in the aliquot, and multiplied by 100, will give the "alkalinity ratio."

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[1] Read at the 57th Meeting of the American Chemical Society at Buffalo, N. Y., April 7 to 11, 1919.

[2] L. L. Van Slyke and A. W. Bosworth, *J. Biol. Chem.*, **20** (1915), 151.

[3] *Ibid.*, **24** (1916), 191.

[4] A. W. Bosworth and M. J. Prucha, *Ibid.*, **8** (1910), 479.

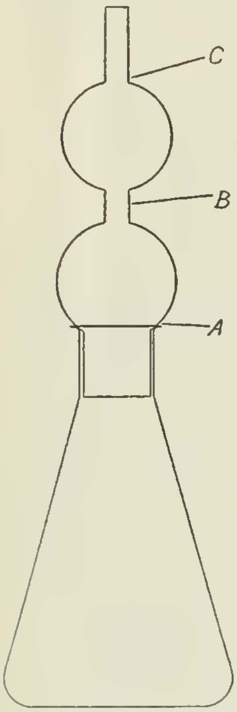

Fig. 1

FOR CREAM, MILK, OR BUTTERMILK—The procedure is the same as for butter, except that a smaller sample must be taken and the fat need not be removed before adding the hydrochloric acid and picric acid. For milk, buttermilk, or thin cream, use a 15 g. sample; for thick cream, 25 g.; for evaporated milk, 7 g.; and for dry milk, 1 g.

Preliminary experiments showed that none of the inorganic salts or the hydrochloric acid were lost during the extraction with ether, but that all of the picric acid and practically all of the lactic acid was removed.

In the experiments given in Tables I and III the samples of cream, from which some butters were made, were brought to the Denver Laboratory of the Bureau of Chemistry in connection with a special project conducted by Dr. H. W. Redfield. The samples reported in Tables II, IV, V, and VI were manufactured in creameries in the vicinity of Denver. In the experiments given in Table VII the samples of butter were made at the experimental creamery of the Dairy Division of the Department of Agriculture. The history of the creams from which the other butters reported were made is not known.

By comparing the results of Expts. 1 and 2 with Expts. 22 and 23, Table I, it appears that the alkalinity ratio varies little, if any, in fresh raw cream from that in rancid and very sour creams that have not been neutralized.

Comparison of Expt. 5, Table I, and Expt. 2, Table II, shows the alkalinity ratio to be the same in the butter and in the unneutralized cream.

TABLE I—ALKALINITY RATIO IN NORMAL CREAM

No.	Description of Sample	Alkalinity Cc. 0.1 *N* per 100 G.	Inorganic P_2O_5 Per cent	Ratio: Cc. *N* Sol. per G. P_2O_5
1	Sweet, raw	46.24	0.0900	51.4
		46.24	0.0936	49.4
2	Sweet, raw	51.81	0.1022	50.7
3	Sweet, pasteurized	50.96	0.0995	51.2
4	Sweet, pasteurized, with starter	52.45	0.1075	48.8
		52.11	0.1086	48.0
5	Sweet, pasteurized, with starter	43.02	0.0985	43.7
		45.44	0.0970	46.8
6	Good	32.02	0.0679	47.2
		30.40	0.0666	45.7
7	Composite first grade	43.40	0.0906	47.9
		44.80	0.0903	49.6
8	Composite first grade	48.10	0.0919	52.3
		46.25	0.0868	53.3
9	Sour, second grade	39.20	0.0716	54.7
10	Sour	51.31	0.0896	57.3
11	Sour	42.57	0.0857	49.7
		42.19	0.0851	49.6
12	Sour	42.25	0.0802	52.6
		41.19	0.0780	52.8
13	Sour, raw	38.49	0.0875	44.0
		37.52	0.0865	43.4
14	Sour, raw	44.87	0.0918	48.9
		48.27	0.0881	54.8
15	Sour, greasy flavor	40.95	0.0871	47.0
		43.74	0.0875	50.0
16	Yeasty and foamy	48.78	0.0914	53.4
		45.42	0.0932	48.7
17	Vinegar	63.41	0.01046	60.6
		61.59	0.01066	57.7
18	Stale	25.26	0.0627	40.3
		31.17	0.0625	50.0
19	Yeasty	51.46	0.0837	61.4
		46.17	0.0892	51.8
20	Aged	42.07	0.0797	52.8
		41.71	0.0807	51.7
21	Stale and cheesy	40.99	0.0868	47.2
		38.46	0.0892	43.1
22	Rancid and yeasty	39.30	0.0927	42.4
		48.70	0.0900	54.1
23	High acid	51.46	0.0949	54.3
		49.36	0.0920	53.7
24	Greasy	41.26	0.0671	61.5
		42.08	0.0612	68.7
25	Too pcor for butter making	38.10	0.0653	58.3
		37.69	0.0632	59.6

The results reported in Table III show among themselves wide variation according to the amount of neutralizer added. The alkalinity ratio is always higher than where no neutralizer is used, even in Expt. 4 where the amount of neutralizer was known to be very small. In the case of Expt. 5, the alkalinity ratio is about three times that recorded in Expt. 24, Table I, the highest ratio found for unneutralized cream.

TABLE II—ALKALINITY RATIO IN BUTTER FROM NORMAL CREAM

No.	Description of Sample	History	Alkalinity Cc. 0.1 *N* per 100 G.	Inorganic P_2O_5 Per cent	Ratio: Cc. *N* Sol. per G. P_2O_5
1	Fresh	....	7.65	0.0170	45.0
			7.67	0.0168	45.5
	In ice box one month	....	7.40	0.0179	41.4
			7.60	0.0182	41.8
	In cold storage one month	....	7.34	0.0178	41.2
			7.77	0.0179	43.3
2	Fresh	Butter from cream analyzed in No. 5, Table I	5.08	0.0121	41.9
			4.66	0.0123	37.9
	In ice box one month	....	6.55	0.0132	49.7
			6.67	0.0129	51.6
	In cold storage one month	....	5.77	0.0124	46.3
			5.61	0.0123	45.9

The results recorded in Table IV are grouped for comparison in Table V, where the alkalinity ratio of a given butter is compared with the cream from which it is made.

The following formula will give an estimation of the acidity reduced in butter and in allied products:

$$A = \frac{P(R - 45)}{11.11}$$

when A = per cent lactic acid reduced, P = per cent P_2O_5 in cream, or milk, and R = ratio on sample.

When this formula is applied to butter and the P_2O_5 content of the cream from which the butter was

TABLE III—ALKALINITY RATIO IN NEUTRALIZED CREAM

No.	Description of Sample	Alkalinity Cc. 0.1 *N* per 100 G.	Inorganic P_2O_5 Per cent	Ratio: Cc. *N* Sol. per G. P_2O_5
1	No. 12, Table I, neutralized	144.9	0.0784	184.8
		145.3	0.0796	182.6
2	No. 12, Table I, neutralized, pasteurized	113.0	0.0799	141.3
		113.8	0.0789	144.1
3	No. 12, Table I, neutralized, pasteurized. Starter added	145.3	0.0825	176.2
		143.8	0.0852	168.8
4	Composite first grade	66.98	0.0890	75.3
		68.44	0.0865	79.1
5	Composite second grade	124.3	0.0670	185.5
		132.2	0.0685	193.1
6	No. 13, Table I, neutralized	89.85	0.0906	99.1
		84.68	0.0917	92.3
7	No. 14, Table I, neutralized	107.9	0.0994	108.4
		99.76	0.1036	96.4

made is not known, an average figure must be taken and only an approximation of the amount of acid reduced in the cream can be made.

In the case of Expts. 1 and 4, Table VI, the per cent acid reduced, as calculated by the formula, is shown to approximate the per cent determined by the acidity test before and after neutralization.

Butter made from partially neutralized cream generally has a higher ratio for a given amount of neutralizer added than butter made from cream completely neutralized. The changes that take place during churning are probably as follows: When the completely neutralized cream is churned, the insoluble di- and tricalcium phosphates would collect during the churning and remain with the butter, while the soluble salts would be partially washed away. The proportion of calcium phosphate to the other salts in the butter then would be higher than in the cream. If this were the case, the ash from such a butter would have a lower alkalinity-P_2O_5 ratio, the ratio being 28 for tri- and 14 for dicalcium phosphate, and at the same time the per cent CaO in the salt-free ash would be higher than found in the cream from which the butter was made. On the other hand, if the cream contained sufficient lactic acid to dissolve the calcium phosphate forming soluble calcium lactate and phosphoric acid or soluble calcium acid phosphates, during the churning and washing of the butter all the salts would be removed in practically the same proportion. Then the alkalinity-P_2O_5 ratio would be higher and the CaO in the salt-free ash lower than in the butter churned from the completely neutralized cream (Samples 18 to 23, Table VII).

TABLE IV—ALKALINITY RATIO IN BUTTER FROM NEUTRALIZED CREAM

No.	Description of Sample	History	Alkalinity Cc. 0.1 *N* per 100 G.	Inorganic P_2O_5 Per cent	Ratio: Cc. *N* Sol. per G. P_2O_5
1	Fresh	Sour cream neutralized	22.99	0.0167	138.1
			23.42	0.0168	139.3
	In ice box one month	....	21.63	0.0179	120.8
			21.50	0.0177	121.7
	In cold storage one month	....	23.31	0.0171	136.2
			22.93	0.0176	130.5
2	Fresh	From cream analyzed in No. 3, Table III	16.34	0.0126	129.4
			16.54	0.0123	134.1
	In ice box one month	....	17.03	0.0120	141.9
			17.89	0.0132	136.0
	In cold storage one month	....	18.37	0.0122	150.5
			17.38	0.0122	142.1
3	Fresh	From cream analyzed in No. 5, Table III	16.90	0.0099	171.6
			16.90	0.0092	183.2
	In ice box one month	....	23.20	0.0105	220.4
			22.84	0.0103	221.8
	In cold storage one month	....	18.14	0.0100	181.2
			17.97	0.0109	165.3
4	Fresh	From cream analyzed in No. 6, Table III	12.03	0.0130	92.4
			11.83	0.0128	92.3
	In ice box one month	....	11.99	0.0113	105.8
			12.09	0.0117	103.4
	In cold storage one month	....	12.12	0.0112	108.0
			11.89	0.0112	106.2
5	Fresh	From cream analyzed in No. 7, Table III	15.94	0.0160	99.6
			15.64	0.0151	103.6
	In ice box one month	....	16.12	0.0144	111.9
			15.89	0.0142	111.8
	In cold storage one month	....	14.92	0.0139	107.6
			15.95	0.0135	118.4
6	Fresh	Source unknown	16.21	0.0181	89.7
7	Fresh	Source unknown	15.31	0.0189	81.1
			15.51	0.0187	83.1
	In ice box one month	....	15.49	0.0168	92.5
			15.49	0.0160	97.1
	In cold storage one month	....	14.80	0.0161	92.0
			15.49	0.0163	95.1

TABLE V—SHOWING ACIDITY AND ALKALINITY RATIO IN SAMPLES OF NEUTRALIZED CREAM AND OF BUTTER FROM EACH CREAM

		ALKALINITY RATIO			
No.	Acidity[1] of Cream when Churned	Cream	Fresh Butter	Butter in Ice Box One Month	Butter in Cold Storage One Month
1	0.21	173	132	139	146
2	0.65	77	72	82	80
3	0.48	189	177	221	173
4	0.32	96	92	105	107
5	0.83	102	102	112	113

[1] These determinations for acidity were made by Mr. W. H. Cole.

A quantity of cream was neutralized with calcium sucrate, pasteurized, and divided into two portions: one-half churned at an acidity of 0.08 per cent lactic acid, and the other half ripened to 0.35 per cent and churned. Samples from each churning were taken after the first, the second, and the third washings. The analyses showed that there was very little difference between the butter washed once and that washed three times. However, the butter from the completely neutralized cream contained more than twice as much CaO and had a lower alkalinity-P_2O_5 ratio than the butter from the partially neutralized cream. As will be seen from Samples 13 to 16, Table VII, the alkalinity-P_2O_5 ratio in butter from cream containing as high as 0.52 per cent acid neutralized may not be any higher than in butter from unneutralized cream, yet the CaO in salt-free ash in those cases was found to be much higher than in butter from unneutralized cream.

TABLE VI—PER CENT ACID NEUTRALIZED

		CALCULATED FROM FORMULA			
No.	Difference in Titration before and after Neutralization of Cream	Cream	Butter	Butter in Ice Box One Month	Butter in Cold Storage One Month
1	0.85	0.97	0.66	0.71	0.76
2	..	0.25	0.21	0.29	0.27
3	..	0.88	0.80	1.01	0.78
4	0.46	0.42	0.38	0.49	0.51
5	..	0.52	0.52	0.60	0.62

To determine whether there were any substances left in solution after extraction with ether that would affect the indicator, the procedure was modified as follows: To the picric acid-free solution enough 0.1 *N* sodium hydroxide solution was added to neutralize exactly the hydrochloric acid in the aliquot. The residue left on evaporating to dryness was ignited at a heat just below redness. If there was much sodium chloride present, as in salted butter, it was necessary to raise the temperature very gradually to prevent loss by decrepitation. The ash was dissolved in 0.1 *N* HCl, the solution filtered from the carbon remaining, and the excess hydrochloric acid titrated as before.

Results were obtained with eighteen of the samples of cream in Table I. The alkalinity was higher in a few cases, but generally lower, and the P_2O_5 consistently higher by the modified procedure. On the different samples the increase in P_2O_5 varied from 8.3 to 27.3 per cent of the amount determined by the original procedure, causing a lowering of the ratio varying from

2.6 to 23.2 on the unneutralized, and from 11.7 to 33.4 on the neutralized cream. Results on one sample of butter from Table II and twenty-two samples of salted butter from Table VII agreed very well with those by the original procedure. Another sample of salted butter showed practically no change in the ratio by the modified procedure after being kept in cold storage for one year. On the other hand, three samples of unsalted butter were examined at different intervals, and the inorganic P_2O_5 by the modified procedure was found to increase very rapidly. In one sample of unsalted butter from ripened cream the inorganic P_2O_5 increased from 0.0261 to 0.0435 per cent on being kept in the ice box for 1 mo. and 13 days, causing the alkalinity ratio by the modified procedure to decrease by 17. However, the P_2O_5 as determined by the original procedure without ignition was found to remain the same. It is evident, then, that as the unsalted butter decomposed some soluble phosphorus compounds were formed, which were converted into inorganic phosphates by ignition and by combining with the bases caused the alkalinity to be lower and the inorganic phosphoric acid to be increased. Therefore, the ratio as determined by titrating the acid solution of the inorganic salts without neutralization and ignition comes nearer to expressing the true alkalinity-P_2O_5 ratio of the butter.

TABLE VII

No.	Per cent Acid Reduced in Cream by Neutralizer[1]	Times Butter Was Washed	Acidity of Cream when Churned	Alkalinity Cc. 0.1 *N* per 100 G.	Inorganic P_2O_5 Per cent	Ratio: Cc. *N* Sol. per G. P_2O_5	CaO[2] in Salt-free Ash
1	0.0	1	0.48	9.24	0.0192	48.2	20
				9.04	0.0195	46.4	
2	0.0	5	Sweet	5.99	0.0126	47.7	..
				5.87	0.0126	47.2	
3	0.0	0	0.44	19.43	0.0435	44.7	23
				19.87	0.0431	46.2	
4	0.17	1	0.41	9.32	0.0157	59.2	18
				9.26	0.0159	58.4	
5	0.18	1	0.22	12.60	0.0291	43.3	24
				12.82	0.0285	45.0	
6	0.20	1	0.31	16.06	0.0277	58.0	28
				16.22	0.0277	58.6	
7	0.26	1	0.34	15.63	0.0300	52.0	34
				15.56	0.0298	52.3	
8	0.30	1	0.24	13.39	0.0185	72.5	30
				12.55	0.0191	65.6	
9	0.31	1	0.29	16.79	0.0286	58.8	31
				16.15	0.0287	56.3	
10	0.32	1	0.28	12.73	0.0175	72.6	22
				12.73	0.0177	72.1	
11	0.36	1	0.24	16.27	0.0273	59.6	33
				16.59	0.0269	61.6	
12	0.38	1	0.26	18.07	0.0243	74.2	32
				17.39	0.0253	68.6	
13	0.42	1	0.20	26.07	0.0522	49.9	40
				26.13	0.0523	49.9	
14	0.47	1	0.16	23.39	0.0508	46.0	39
				23.59	0.0501	47.1	
15	0.57	1	0.15	37.90	0.0828	45.8	46
				37.90	0.0832	45.6	
16	0.52	6	0.18	23.07	0.0425	54.2	43
				22.07	0.0431	51.2	
17	0.52	6	0.18	22.09	0.0401	55.1	38
				21.76	0.0409	53.2	
18	0.57	1	0.08	46.71	0.0714	65.2	43
				46.47	0.0716	65.0	
19	0.57	2	0.08	46.15	0.0694	66.5	45
				45.09	0.0700	64.4	
20	0.57	3	0.08	42.83	0.0676	63.3	45
				42.95	0.0676	63.5	
21	0.57	1	0.35	22.59	0.0306	73.8	39
				22.26	0.0306	72.7	
22	0.57	2	0.35	22.67	0.0305	74.4	41
				22.60	0.0305	74.2	
23	0.57	3	0.35	22.15	0.0274	80.9	37
				21.46	0.0275	78.1	

[1] Lime was used as a neutralizer on Samples 5 to 23, and KOH on Sample 4.

[2] The determinations of calcium oxide were made by Mr. O. L. Evenson, of this laboratory.

SUMMARY

A method has been devised for obtaining the ratio of the alkalinity of the salts to the inorganic phosphoric acid of cream, butter, buttermilk, and milk. This ratio varies within definite limits with milk and cream and is increased in neutralized cream or milk, the increase being in proportion to the amount of neutralizer added. The butter from neutralized cream gave a ratio similar to that of the cream, when it was churned at an acidity of 0.3 per cent or over. However, when lime was used as a neutralizer and the cream churned witt an acidity of less than 0.3 per cent in a few cases the alkalinity-P_2O_5 ratio was not increased, although the CaO in the salt-free ash in these particular samples was unusually high. This is explained as being due to the occlusion of insoluble calcium phosphate.

A formula is given for calculating the per cent of acid neutralized in a sample of cream or milk which can be applied to butter when the phosphoric acid content of the cream from which the butter was made is known. An approximate estimation of the neutralizer in the butter can be made without knowing the phosphoric acid content of the cream by taking an average figure. Five samples of cream and the corresponding samples of butter were calculated by the formula to contain from 0.2 to 1.0 per cent of neutralized lactic acid.

Tables are given showing results with twenty-five samples of unneutralized cream, with seven samples of neutralized cream, with nine samples of butter from unneutralized cream, and with twenty-eight samples of butter from neutralized cream.

Appreciation is expressed to Dr. I. K. Phelps, chemist in charge of this laboratory, for valuable direction.

THE HEAT OF HYDRATION AND SPECIFIC HEAT OF WHEAT FLOUR

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In general bakery practice it is conceded that a dough set at a temperature of from 80° to 82° F. produces bread of the best quality. After a standard period of 5 hrs. fermentation, a dough set at this temperature will have a temperature of about 86° F. A lower temperature produces a dough which ferments slowly and a higher temperature one which ferments too rapidly.

The two main ingredients in bread are flour and water. All the other ingredients are so small in comparison that they may be neglected in a consideration of the temperature involved. In making a dough the three temperatures which are vital are those of the flour, the room, and the water. The first two are more or less inflexible, but that of the water is very easily adjusted. Accordingly, no attempt is made to change the temperature of the flour or the room within certain limits, but that of the water is made proportionally higher or lower in order to make the dough of the required temperature.

The purpose of the experimental work outlined in this paper is primarily to establish the relationship of the temperature of the flour and water to the resultant dough and to compare this relationship with empirical formulas in general use in the baking industry.

In ordinary mixtures the specific heats of the substances and the law of mixtures can be applied, but in bread making these are not sufficient to explain the empirical formulas and rule-of-thumb calculations which are in use in bakeries. In the present investigation it was found that the heat evolved when water acts upon flour is so great that it must be included in any calculations for dough temperature.

EXPERIMENTAL

SPECIFIC HEAT OF FLOUR—The specific heat of flour was determined by packing 300 g. into small watertight copper cylinders of negligible heat capacity. These were kept over night in a thermostat at a slightly elevated temperature, and immediately after removal were submerged in the calorimeter. Although the method involving the transfer of a warm body through the air is not accurate, values of 0.42 and 0.43 were obtained. These values were checked by experiments in which flour at elevated temperatures was mixed directly with the water, allowance being made for the heat of hydration. By combining the data of two such experiments the specific heat was made the only unknown quantity. The average of all the determinations of the specific heat of flour was taken as 0.43. As the moisture content of these flours was about 13 per cent the specific heat of moisture-free flour would be about 0.34. Jago[1] obtained values of 0.40 to 0.53 in laboratory experiments without taking into consideration the heat of hydration or the heat absorbed by the containing vessels. On machine-mixed doughs he obtained values of 0.30 to 0.45 without consideration of the heat of hydration, the heat absorbed by the mixers, or the mechanical heat generated in the mixture.

HEAT OF HYDRATION—The heats of hydration were determined experimentally by mixing flour and water in an adiabatic calorimeter in which cooling corrections were eliminated. The calorimeter was constructed of copper cans surrounded by a water jacket. The temperature was kept within 0.1° to 0.2° of the temperature of the dough, as registered by a thermocouple. Heat was introduced into the jacket, as required, by the operation of a switch in a circuit of a 110 volt alternating current which passed through the water of the jacket by electrolytic conduction.[2]

After several experiments it was found that a mixture of two parts of water to one of flour was the most concentrated which would give satisfactory results. With this proportion the mixing was rapid and complete, and the temperature attained a permanent maximum in a few minutes. In more concentrated mixtures stirring was mechanically difficult and an inconveniently long time was required to attain the maximum temperature. Experiments showed that the heat of hydration was practically independent of the concentration. In the case of very stiff doughs, however, the full heat of hydration was registered only after a considerable time.

One experiment on a straight grade of flour is sufficient to illustrate the calculations involved. Three hundred grams of flour at 25.26° C. were added to 600 g. of water at 23.97° C. in the calorimeter. The temperature rose to 25.69° C. within 10 min. and remained constant. The heat of hydration was 1.72° (600 × 1.00 (sp. heat water) + 35 (water equivalent of calorimeter)) + 0.43° (300 × 0.43 (sp. heat flour)) = 1148 cal. Dividing by 300 gives 3.83 cal. per gram, the heat evolved when flour of this kind is mixed with water. In a check determination flour at 25.61° C. and water at 23.82° C. gave dough at 25.60° C., from which the value 3.77 cal. per gram is obtained. Multiplying by $^9/_5$ gives 6.89 and 6.78 B. t. u. per pound.

The greatest source of error in the experiments on the heats of hydration lay in determining the temperature of the flour. A powder-like flour is an excellent heat insulator and a thermometer plunged into it is very slow to register, and gives the temperature in the immediate vicinity only, whereas another portion may differ considerably, depending on recent changes in the room temperature. Toward the last of the investigation the sample of flour was thoroughly mixed by shaking in a large bottle just before the insertion of the thermometer. It would have been better to keep the temperature of the room absolutely constant for a long time previous to the determination or to keep the flour in a thermostat. In spite of the difficulty of getting the true average temperature of the flour duplicate experiments checked within 0.1 cal. per gram in nearly all cases.

The results are summarized in Table I, where Column 5 gives the heat of hydration in calories per gram as determined in June 1916; Column 6 the heat of hydration as given in Column 5 expressed in B. t. u. per lb.; Column 7 the heat of hydration in calories per gram as determined in September 1916, after storage in glass bottles; and Column 8 the heat of hydration as given in Column 7 expressed in B. t. u. per pound.

TABLE I—HEAT OF HYDRATION OF WHEAT FLOUR

GRADE	SOURCE	Wet Gluten	Dry Gluten	June		September	
				Cal.	B.t.u.	Cal.	B.t.u.
Low Grade	Manitoba Spr.	32.0	3.33	4.23	7.62	4.19	7.54
Straight	Manitoba Spr.	..	...	4.00	7.20	3.80	6.84
2nd Bakers	Manitoba Spr.	33.0	12.00	3.89	7.00	3.76	6.77
1st Bakers	Manitoba Spr.	29.6	11.33	3.68	6.62	3.66	6.59
1st Clear Spring	Minnesota Spr.	28.3	12.06	3.64	6.55	3.57	6.43
Fancy Family Spring	Minnesota Spr.	26.6	9.83	3.41	6.14	3.38	6.08
Hard Wheat Clear	Kan. Hd. Wtr.	30.0	10.63	3.26	5.87	3.20	5.76
Patent Hard Wheat	Kan. Hd. Wtr.	28.6	10.00	3.36	6.05	3.01	5.42
Winter Wheat Straight	Ontario Wtr.	20.0	7.00	3.23	5.82	3.01	5.42

From an examination of the table it is evident that the heat of hydration of flour depends to a certain extent on its wet gluten content. Unfortunately there was a delay of a few months between the time of milling and the experimental determinations, so that the results are not as significant as could be desired. The differences between the June and September determinations, although small, point to a very slight deterioration even when kept in glass-stoppered bottles. During the same period "Low Grade" stored in an open sack fell from 7.62 to 5.62 B. t. u. per lb.; "First Bakers" in an open sack fell from 6.62 to 5.08, and "Second Bakers" when exposed in an open sack fell only from 7.00 to 6.30 between July 1916 and July 1917.

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[1] "Technology of Bread Making," pp. 5, 6.

[2] *J. Am. Chem. Soc.*, **38** (1916), 1473.

To study the effect of age on the heat of hydration, samples, of practically the same gluten and moisture content, were preserved in airtight, light-tight tins at the time of milling. The results in B. t. u., of calorimetric determinations made in July 1917 are given in Table II.

TABLE II—INFLUENCE OF AGE ON HEAT OF HYDRATION

DATE OF MILLING	Heat of Hydration	DATE OF MILLING	Heat of Hydration
April 10, 1916	3.82	Jan. 10, 1917	5.78
May 10, 1916	4.88	Mar. 10, 1917	4.47
June 10, 1916	4.02	Apr. 10, 1917	3.98
Sept. 10, 1916	4.77	May 10, 1917	3.89[1]
Nov. 10, 1916	4.36	June 28, 1917	3.71

[1] This sample was kept in a paper sack.

There is no marked evidence of decreasing heat of hydration with age under these conditions, where the flour is effectively protected from external conditions. The results seem rather discordant but there is a pronounced difference between the winter and summer samples and there is a fair agreement between the same months of the two years. There is almost enough evidence to lead to the conclusion that the heat of hydration of a flour of constant composition varies inversely as the humidity at the time of milling. Further investigation is needed to explain fully these variations, as well as the further change which takes place when exposed to atmospheric conditions. It appears likely that the rather high heat of hydration of freshly milled flour depends largely on the gluten content, but that the gluten is partially hydrated on standing. The higher the humidity, the greater is this partial hydration. It is so great that freshly milled flour has to age several weeks, during which time it is continuously warmer than its surroundings. After this aging period further hydration takes place only when exposed to external moisture, and the extent of hydration depends on the humidity and on the degree of exposure. After exposure of many months to the atmosphere further exposure has very little effect, even though the heat of hydration may still be considerable.

CALCULATION OF DOUGH TEMPERATURES

For the calculation of dough temperatures the law of mixtures may be used if a proper correction is made for the heat of hydration. A simple formula may be derived on the basis of the following relation:

Heat evolved = wt. flour × ht. of hydration per unit of wt. = (wt. flour × temp. rise flour × sp. ht. flour) + (wt. water × temp. rise water × sp. ht. water)

Expressed in the corresponding symbols the relation becomes:

$$W_fH_h = W_fR_fS_f + W_wR_wS_w \qquad (1)$$

For a typical dough of 60 lbs. of water and 100 lbs. of flour, of specific heat 0.43 and heat of hydration 6.5 B. t. u. per lb., Equation 1 becomes:

$$(100 \times 6.5) = R_f\,(100 \times 0.43) + R_w\,(60 \times 1) \qquad (2)$$

$$R_w = -0.7R_f + 11 \qquad (3)$$

For the special case where the final temperature of the dough is 80° F. the rise in temperature in each case (R_w or R_f) is equal to the difference between 80° F. and the original temperature of the water or the flour: $R_w = 80 - T_w$ and $R_f = 80 - T_f$.

Substituting in (3):

$$80 - T_w = -0.7\,(80 - T_f) + 11 \qquad (4)$$

$$T_w = 125 - 0.7\,T_f \qquad (5)$$

The temperature of the water which will give a dough of 80° F. may thus be found by subtracting 0.7 of the temperature of the flour from 125. Slight changes in the numerical constants are needed in case the flour does not have a heat of hydration of 6.5 B. t. u. per pound. For a low-grade flour with a heat of hydration of 7.6 B. t. u. the formula becomes $T_w = 123 - 0.7\,T_f$, while for a winter wheat with a heat of hydration of 5.4 B. t. u. it becomes $127 - 0.7\,T_f$.

This formula is an "ideal" one and does not hold under practical working conditions, which are complicated by the heat of stirring and the exchange of heat with the room and with the mixer. The last two quantities become negligible if the room temperature is close to 80° F. The heat of stirring, which is large, depends on the speed of the mixer. These quantities should be determined experimentally under working conditions. They must be included in a completely general expression, which may be obtained by expanding Equation 1 as follows:

$$W_fH_h = W_fS_fR_f + W_wS_wR_w - H_m - H_e \qquad (6)$$

where H_m is the mechanical heat generated in mixing, and H_e is the heat absorbed from the environment.

Combining as before for the typical dough:

$$R_f\,(100 \times 0.43) = -R_w(60 \times 1) + W_fH_h + H_m + H_e \qquad (7)$$

For practical use it is best to group the last three terms into one quantity, K, which may then be determined on a large scale under working conditions. It depends on the heat of hydration, the speed of mixing, and the temperature of the room, but is constant when these are constant.

Substituting K for the three last terms in (7) and simplifying

$$R_w = -0.7\,R_f + K. \qquad (8)$$

To show how Equation 8 may be used in the bakery, suppose that 100 lbs. of flour at 70° F., were mixed with 60 lbs. of water at 76° F., but that the final temperature was 84° instead of 80°, as expected from the "ideal" formula (5) because of the extra heat due to mechanical stirring. The value of K is found by substituting the proper values in Equation 8, thus:

$$(84 - 76) = -0.7\,(84 - 70) + K \qquad (9)$$

$$K = 18 \qquad (10)$$

Having determined K, it can now be used in all cases where the conditions are the same by substituting its numerical value in Equation 8.

For the special case of an 80° dough:

$$(80 - T\ ) = -0.7\,(80 - T_f) + 18 \qquad (11)$$

$$T = 118 - 0.7T_f \qquad (12)$$

Solving Equation 12 for the example just given it is found that if the flour is at 70° the water should be at 69° to give a dough at 80°. Equation 12 will give the proper temperature of the water over the whole range when the bakery conditions are the same as when K was determined.

As a short cut it is convenient to note that to change the temperature of the dough by 1° it is necessary to change the temperature of the water in the same direction by 1.7° C., for

$$\frac{(100 \times 0.43 + 60 \times 1)}{60 \times 1} = 1.7^\circ.$$

Another variable lies in the fact that in thick doughs the flour may not have time to become fully hydrated in the mixing process. If such is the case the heat evolved up to the time of setting the dough will be less than that given in the tables used in the formulas. However, in the formula for practical use (Equation 8) this source of error is absorbed in the constant K.

COMPARISON WITH EMPIRICAL RULES

It is of interest to examine empirical rules which are now in common use and compare them with the formulas just given. The simplest one averages the temperature of the flour and the water to give the final dough temperature. If this is to be 80°, 2 × 80° minus the temperature of the flour gives the required temperature of the water. This is possible as an approximation because the heat capacities of the two chance to be roughly equal, 60 × 1.0 and 100 × 0.42.

An improved formula averages the temperature of the room with that of the flour and the water, thereby making an approximate but wholly empirical correction for exchange of heat with the environment. Tables[1] made up from this rule and copyrighted in 1912 have been widely used. When the room temperature is close to 80° F. the latter rule has no advantage over the former. Neither takes into consideration the heat of hydration, and the error is shown by the fact that if the flour and water, both at 80° F., are mixed in a room at 80° with negligible heat of stirring, the dough temperature for a straight grade of flour will not be 80° as given by the rules, but nearly 84° F.

A third formula corrects for the heat of hydration by arbitrarily subtracting 10° from the sum of the temperatures of the flour and the water. Thus if the dough is to be 80°, 150 (2 × 80 — 10) is the quantity from which the temperature of the flour must be subtracted to obtain the proper temperature for the water. By a fourth rule 12° is subtracted from the sum of the temperatures of the flour, the room, and the water.

A comparison of the different rules is shown in Table III, where Column 1 gives the temperature of the flour, Column 2 the temperature of the room (calculated only for 80° and 70°), and the succeeding columns the temperature of the water which will give an 80° dough according to the formulas already discussed.

It is evident from a comparison of the different columns that there is a wide discrepancy in the results obtained by the various rules which are used by bakers. It is common practice to have the water too cold and bring the dough up to the proper temperature by longer or shorter operation of the mixing machine. In the case of high-speed mixers, particularly, a rapid rise in the temperature results from the mechanical heat generated.

TABLE III—CALCULATION OF WATER TEMPERATURES FOR AN 80° F. DOUGH

FLOUR ° F.	ROOM ° F.	$(T_w = 160 - T_f)$	$(T_w = 240 - T_f - T_r)$	$(T_w = 150 - T_f)$	$(T_w = 228 - T_f - T_r)$	$(T_w = 125 - 0.7\ T_f)$
60	80	100	100	90	88	83
60	70	...	110	..	98	..
62	80	98	98	88	86	81.6
62	70	...	108	..	96	..
64	80	96	96	86	84	80.2
64	70	...	106	..	94	..
66	80	94	94	84	82	78.8
66	70	...	104	..	92	..
68	80	92	92	82	80	77.4
68	70	...	102	..	90	..
70	80	90	90	80	78	76.0
70	70	...	100	..	88	..
72	80	88	88	78	76	74.6
72	70	...	98	..	86	..
74	80	86	86	76	74	73.2
74	70	...	96	..	84	..
76	80	84	84	74	72	71.8
76	70	...	94	.	82	..
78	80	82	82	72	70	70.4
78	70	...	92	..	80	..
80	80	80	80	70	68	69.0
80	70	...	90	..	78	..
82	80	78	78	68	66	67.6
82	70	...	88	..	76	..
84	80	76	76	66	64	66.2
84	70	...	86	..	74	..
86	80	74	74	64	62	64.8
86	70	...	84	..	72	..
88	80	72	72	62	60	63.4
88	70	...	82	..	70	..
90	80	70	70	60	58	62.0
90	70	...	80	..	68	..
92	80	68	68	58	56	60.6
92	70	...	78	..	66	..

All the figures except those in Column 7 are obtained by purely empirical rules. Although based on scientific experiment, the figures in Column 7 hold only for "ideal" conditions in which the room temperature is close to 80° F. and the heat generated by mechanical mixing is negligible. For practical use in bakeries the formula for "ideal" conditions must be modified as shown in Equations 7 to 12 with the help of data taken under actual working conditions.

SUMMARY

1—The heat of hydration of various wheat flours has been found to range from 7.6 B. t. u. per lb. in a low grade to 5.4 B. t. u. per lb. in a winter wheat flour. For a straight grade, such as has been used chiefly in bakeries, 6.5 B. t. u. per lb. was found to be a good average.

2—The heat of hydration decreased on exposure to the atmosphere, but did not change appreciably with age when completely isolated from the air.

3—The true specific heat of wheat flour was found to be 0.43.

4—Both specific heat and heat of hydration must be considered in any calculation of dough temperatures.

5—Empirical rules for dough temperatures have been discussed and a scientific formula has been proposed, together with suggestions for its application to the baking industry.

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[1] Washburn-Crosby Dough Sheet F. 1.

THE KREIS REACTION OF COTTONSEED-OIL PRODUCTS

By W. B. Smith

Armour and Company, Kansas City, Kansas

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The Kreis test for rancidity, consisting of shaking a fat or oil with equal volumes of hydrochloric acid and phloroglucinol-ether solution, has come into use in this country as a means of determining the fitness of the fat for food. It is fully described by Kerr,[1] who mentions among its limitations that it is given by other substances than rancid fats, including the impurities in crude cottonseed oil.

The purpose of this article is to show that not only crude, but also refined cottonseed oils, may give the reaction; and that when the Kreis test is used to decide whether a fat is rancid this natural reaction may cause a mistake to be made.

In the inspection of animal fats there is not the same danger of an erroneous decision as with cottonseed-oil products. In the first place, lard, tallow, etc., do not contain carbohydrates or other impurities such as are found in crude cottonseed oil; and, second, the chemist is aided by free acid, odor, taste, color, and sediment to form a decision as to their soundness. On the other hand, the refining of cottonseed oil with caustic soda removes the free acid and insoluble matter, while the naturally disagreeable taste of the oil masks faint rancidity. Consequently the Kreis test assumes a much greater importance, and is in fact almost the only means of detecting incipient rancidity in cottonseed oil, and any error in making or interpreting the test may have far-reaching results.

Kerr's statements in regard to cottonseed oil are as follows:

> Fresh, sweet fats do not give the reaction except in certain special cases. Such a case is that of crude cottonseed oil, which reacts with great intensity. In this case the substance which causes the reaction is removed by refining with caustic soda.
>
> The Kreis test is not specific for rancid fats. It is given by aldehydes and ketones, other than those which occur in rancid fats, * * * * * by crude cottonseed oil and probably by other crude oils.
>
> In making use of the Kreis test for the detection of rancidity, it is necessary to guard against a reaction due to the presence of any reacting substance, other than those due to rancidity. If such a substance is present any conclusion drawn from a positive reaction is worthless * * * * all animal fats and all refined vegetable oils are free from reacting substances.

As far as the writer has experienced, these statements are correct except in the case of refined cottonseed oil. It is very reasonable to expect that the chromogenetic substances in crude cottonseed oil, which give a Kreis reaction many times stronger than any color produced by rancidity, might pass to some extent into the refined oil. In most cases refined cottonseed oils show a negative Kreis reaction, but there are often found on the market oils which, in color, odor, taste, and appearance are entirely edible, but which give a positive Kreis test strong enough to mislead the chemist into pronouncing them rancid. The importance of a correct diagnosis of a color test which may lead to the condemnation of carloads of edible oil can be readily seen, and for this reason the following experiments are selected from a large amount of work as tending to elucidate the subject.

In order to decide whether a positive Kreis test in a refined cottonseed oil always indicates rancidity, it is necessary to find some reaction of rancid cottonseed oils which is different from that of non-rancid oils. Caustic soda, hydrochloric acid, hydrogen peroxide, etc., all act similarly in both cases.

Lewkowitsch,[1] who has a very poor opinion of color reactions, states:

> Exposure to light destroys those minute traces of chromogenetic substances which give rise to color reactions that were for a long time, erroneously, considered as characteristic. Since pure glycerides are themselves colorless, the light can only affect the foreign substances dissolved in them. This is further proved by the fact that insolated cottonseed oil does not reduce silver nitrate so readily as does cottonseed oil kept in the dark.

On the other hand, it is well known and easily proved that sunlight does not decrease rancidity as measured by the Kreis test, even if air and moisture be excluded, but increases it. Consequently experiments were begun on the assumption that an increase in the Kreis test after exposure of a sample of oil to direct sunlight would indicate rancidity, while a decrease would indicate natural chromogenetic substances.

EXPERIMENTAL

This assumption was first tested out on crude oils which are acknowledged by Kerr to contain natural chromogenetic substances giving the Kreis reaction. Owing to the intensity of the color developed by pure crude oil, the samples were diluted with lard or other neutral fat. Small bottles were filled with the mixtures, corked tightly, and exposed to the sun for about three weeks, being opened at intervals to determine their Kreis reaction. Table I and the accompanying curve show the results.

These figures prove that mixtures containing from 0.05 to 12.5 per cent of crude cottonseed oil were affected by the sunlight so that the Kreis test decreased uniformly and markedly, until rancidity began to set in, when it increased distinctly but more slowly.

Table I—Effect of Sunlight on Natural Kreis Reaction

	Crude Oil	Kreis Reaction (Expressed in Intensity of Color)								
Mixture	Per cent	Beginning	1 day	2 days	4 days	7 days	10 days	14 days	17 days	20 days
A.....	12.5	400	..	300	200	150	100	75	40	25
B.....	3.1	175	..	125	80	50	35	25	12	20
C.....	1.5	100	..	75	50	30	20	12	2	10
D.....	0.8	60	50	40	35	15	5	6	20	20
E.....	0.4	35	30	20	4	1	2	..	..	..
F.....	0.2	20	12	5	5	10	10	..	..	..
G.....	0.05	5	Trace	2	2	2	7	20	35	..

In other words, by simply exposing these samples in a southern window the Kreis reaction was decreased from an intense purplish red, graded 1 : 400 on Kerr's scale, to a weak red estimated as 1 : 25, in sample A, *i. e.*, 94 per cent of the Kreis-reacting substance disappeared. In the case of Sample C, sunlight changed the oil from a Kreis reaction of 1 : 100 to 1 : 2, *i. e.*, 98 per cent, or all but a mere trace of the chromogenetic substances disappeared. All the other samples showed a similar decrease of the natural Kreis reaction, while that due to rancidity increased considerably in some cases.

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[1] This Journal, 10 (1918), 471.

[1] "Oils, Fats and Waxes," 5th Ed., I, 46.

Although not shown here, certain samples of crude and refined oils originally giving a strong Kreis reaction have been found to give an entirely negative one after exposure to sunlight. Of course this does not usually happen because the exposure produces rancidity before the chromogenetic substances are entirely destroyed.

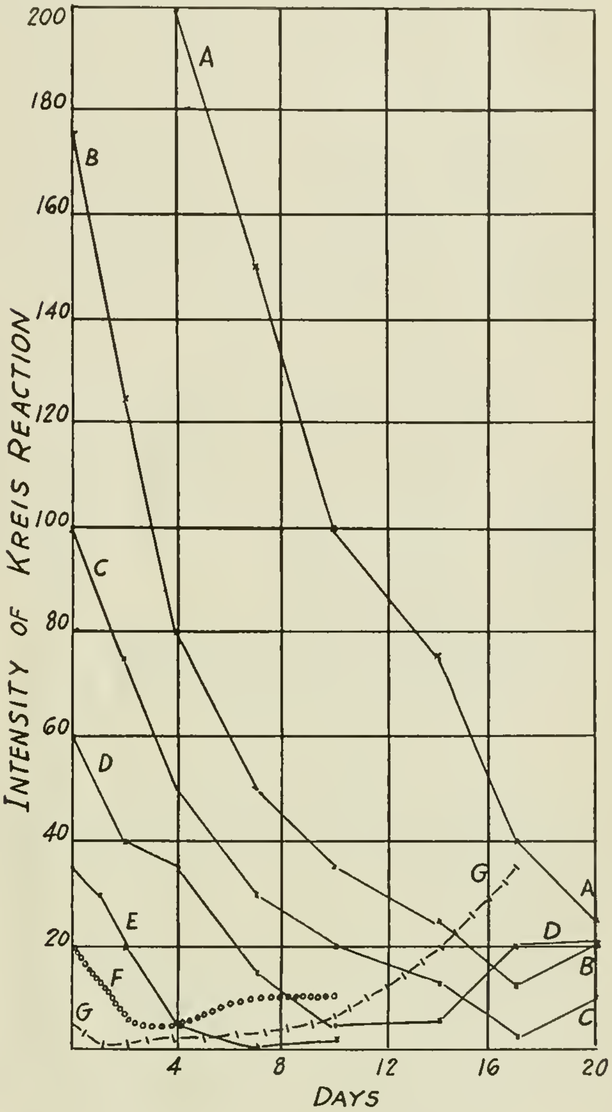
So far these results confirm the researches of Kerr. They indicate that the Kreis reaction in crude cottonseed oil is not at all due to rancidity, and also that exposure to sunlight distinguishes to a certain extent between rancid and non-rancid oils giving a positive Kreis test. This method was therefore applied to commercial fats and oils, both animal and vegetable, some of which were edible and some inedible. Representative results are shown in Table II.

Table II—Kreis Reaction of Commercial Fats and Oils

No.	Composition	Kreis Reaction Untreated Oil	Kreis Reaction Exposed Oil
1	Cottonseed oil refined in laboratory...	1 : 5	1 : 1
2	Cottonseed oil, commercial product.	1 : 7	1 : 3
3	Cottonseed oil, commercial product.	Negative	Negative
4	Cottonseed oil, commercial product.	1 : 4	Trace
5	Cottonseed oil, commercial product.	1 : 2	Negative
6	Cottonseed oil, commercial product.	1 : 3	1 : 1
7	Cottonseed oil, commercial product.	1 : 6	1 : 4
8	Cottonseed oil, commercial product, old..............................	1 : 10	1 : 7
9	Cottonseed oil, inedible, domestic...	1 : 11	1 : 10
10	Cottonseed oil, inedible, Chinese....	1 : 5	1 : 4
11	Cottonseed oil, inedible, off.........	1 : 5	1 : 4
12	Olive oil..........................	1 : 2	1 : 3
13	Olive oil, Spanish..................	1 : 3	1 : 5
14	Olive oil..........................	Negative	Negative
15	Peanut oil.........................	Negative	Negative
16	Crude sesame oil....................	Negative	Negative
17	Crude sesame oil....................	Negative	Negative
18	Crude Tabiti coconut oil...........	1 : 4	1 : 5
19	Refined coconut oil................	Negative	Negative
20	Refined coconut oil................	Negative	Negative
21	Palm oil, rancid...................	1 : 10	1 : 15
22	White grease.......................	1 : 10	1 : 12
23	Peanut oil.........................	1 : 1	1 : 1
24	Tallow, off........................	1 : 1	1 : 2
25	Edible tallow......................	Negative	Negative
26	Neat's-foot oil, rancid............	1 : 3	1 : 4
27	Low-grade lard.....................	Negative	Negative
28	Lard substitute, mixture of cottonseed oil and tallow..............	1 : 8	1 : 5.
29	Compound mixture of cottonseed oil and stearin.....................	1 : 6	1 : 3

The control samples consist of both rancid and non-rancid oils. In all cases (excepting cottonseed) where the original oil gave a positive Kreis reaction, it did not decrease on exposure to sunlight but usually increased. This indicates that with olive, peanut, sesame, coconut, palm, and neat's-foot oils, and white grease, tallow, and lard, a positive Kreis test is due to rancidity; at least, no indication of naturally reacting substances was obtained.

The samples of cottonseed oil shown in the table include most classes of refined oils, but nearly all of them fall into one of two groups, those in which the Kreis test is wholly or partly due to chromogenetic substances, and those in which it is chiefly due to rancidity. All of the samples showed some lessening of the Kreis test after exposure to sunlight, but while in some it is nearly or quite complete, in others it is slight or negligible. Of course, in a really rancid oil the reaction would increase just as in the case of any other vegetable or animal oil. The evidence summarized in this table, therefore, can be explained only on the hypothesis that refined cottonseed oil may give a positive Kreis reaction although it is not rancid. In this respect alone this work disagrees with that of Kerr, who found that "all refined vegetable oils are free from reacting substances."



Effect of Sunlight on Kreis Reaction

The natural Kreis reaction of cottonseed oils is more of a purplish red than the rancidity reaction. It is also more slow to develop, sometimes taking many hours to reach a maximum. As was pointed out by Kerr, the test is so delicate that much care must be taken to avoid false conclusions. For instance, a positive test has been known to be due to the age or quality of the phloroglucinol-ether solution. Again, the oil used as a dilution medium may cause an unsuspected error. In one extreme case a petroleum distillate showing negative to Kreis gave, when mixed in equal proportions with a rancid fat, a more intense color than the fat gave by itself. It was positive in a 1 : 40 dilution, while the substitution of coconut oil for the petroleum caused the reaction to show only 1 : 10. The error appeared to lie in the presence of cracked compounds in the petroleum, which turned brown when allowed to stand with hydrochloric acid, or even in strong sunlight.

Temperature appears to affect the intensity of the color to some extent, so that irregular results may be obtained with such substances as hydrogenated cottonseed oil, which melts at a high temperature.

The natural Kreis-reacting substances in cottonseed oil are not glycerides, and bear no relation to the decomposition of the glycerides, from rancidity or any other cause.

The work from which the above observations have been selected covers a period of eleven years' experience with the Kreis test, during which thousands of samples of edible fats have been examined. The portion which was done recently was carried out with the assistance of Mr. Isaac N. Jordan.

CONCLUSIONS

Refined cottonseed oils and their products sometimes contain chromogenetic substances carried over from the crude oil. These substances sometimes cause a positive Kreis reaction in a non-rancid oil, and hence interfere greatly with the detection of rancidity by this means. For this reason the Kreis test is not entirely dependable for the detection of rancidity in cottonseed oil.

MODIFICATION OF THE HOWARD METHOD FOR COUNTING YEASTS, SPORES, AND BACTERIA IN TOMATO PRODUCTS

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The modification here described is based on the fact that by boiling tomato pulp with Loffler's methylene blue and Ziehl-Neilsen's carbofuchsine the microorganisms are stained a slightly deeper color than the tomato tissues.

Aside from producing this slight differential effect, the combination of the two stains facilitates the observation of the yeasts, spores, and bacteria. Methylene blue, used alone, fails to properly stain some of the organisms, while carbofuchsine, without the addition of methylene blue, produces a reddish color which makes it hard to see clearly the outline of the bacteria when artificial light is used.

Take 20 cc. of tomato juice, pulp, or ketchup, or 5 cc. of paste or other highly concentrated products. Transfer the sample to a 100 cc. beaker using sufficient water to make the total volume about 30 cc. Heat to boiling, and add 2 to 4 cc. of Loffler's alkaline methylene blue. Stir well and continue the boiling for 3 min. The amount of methylene blue used depends on the concentration of the product under examination, enough being added to color the sample blue. A green color shows that insufficient stain has been used.

Next add 2 cc. of Ziehl-Neilsen's carbofuchsine, stir well, and again boil for 3 min. Let cool a minute, and add 5 to 10 drops of formaldehyde to reduce any excess of carbofuchsine; stir well and dilute with water to 60 or 120 cc., depending upon the concentration of the product. Shake well, transfer some of the sample to a beaker, prepare the microscopic slide in the usual manner and examine by the Howard method.[1]

It is necessary to use artificial light since the blue color of the slide makes examination by daylight very difficult.

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[1] Association of Official Agricultural Chemists, Report of Committee on Editing Tentative and Official Methods of Analysis, **1916**, 324.

THE BEHAVIOR OF PHENOLPHTHALEIN WITH IODINE AND A METHOD FOR THE DETERMINATION OF PHENOLPHTHALEIN

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The question has frequently arisen as to the actual therapeutic strength of medicinal preparations containing phenolphthalein. Though phenolphthalein has had widespread use in medicine for many years, no method for its quantitative determination has been found satisfactory.

Among those investigated is a titration method proposed by Kollo,[1] based on the well-known reactions of phenolphthalein with iodine in which tetraiodophenolphthalein[2] is formed Numerous experiments with Kollo's method failed to give concordant results and made it apparent that the reaction was subject to a number of errors, among which oxidation and incompleteness of conversion to the tetraiodo compound were later found to be most important.

In the present investigation a study was made of the effect upon this reaction of varying successively the concentration of iodine, temperature, and concentration of alkali, while that of the phenolphthalein was kept constant.

EXPERIMENTAL

The general method of carrying out the experiments enumerated in Tables I, II, and III consisted quite uniformly in the addition of a solution of iodine in potassium iodide to an aqueous alkaline solution of phenolphthalein. In nearly every case an approximately quantitative estimation of the principal reaction product, tetraiodophenolphthalein, was made by extraction of the reaction mixture with chloroform in a separatory funnel, after the excess of iodine had been removed with sodium sulfite and the whole acidified with hydrochloric acid.

The use of chloroform as an extraction medium was determined upon from a few preliminary experiments with a number of organic solvents immiscible with water. When freshly precipitated with acid from the cold alkaline solution, tetraiodophenolphthalein was found to be readily soluble in chloroform. The color of the weakly alkaline solution of the pure compound is wine-red by transmitted light and blue by reflected light. Phenolphthalein is only sparingly soluble in chloroform and the color of its alkaline solution needs no description.

In each experiment observations were made as to:

(1) The character of precipitate formed.

(2) The character, amount, and color of the alkaline solution of the portion of the precipitate remaining insoluble in chloroform.

(3) Appearance, weight, and color of the alkaline

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[1] *Pharm. Praxis, Bucharest*, **7** (1908), 341.

[2] Classen and Lob, *Ber.*, **28** (1895), 1605.

solution of the residue obtained from the chloroform extract.

SERIES I. VARYING IODINE CONCENTRATION—A number of experiments in which the concentration of iodine was varied while temperature and concentrations of alkali and phenolphthalein were kept constant, gave the following results:

(1) In every case the precipitate was brown and amorphous in form, resembling periodides, and the more iodine added, the darker the precipitate.

(2) There always remained a portion insoluble in chloroform. On further examination this proved to be chiefly unchanged phenolphthalein.

(3) The evaporated residues from the chloroform extractions were yellow to reddish brown, indicating contamination by oxidation products. Pure tetraiodophenolphthalein, as noted later, is nearly white.

(4) These residues obtained from the chloroform extracts, on treatment with potassium hydroxide, gave solutions varying in color from purple to almost red. They were obviously mixtures of tetraiodo compound and unchanged phenolphthalein in varying proportions. As shown in Table I, A and B, the weights of the chloroform-soluble residue for each set varied only slightly.

TABLE I—EFFECT OF VARIATION OF IODINE CONCENTRATION[1]

		Phenolphthalein Solution 10 cc.	Conc. Iodine Solution Per cent	$CHCl_3$-Insol. Portion	Dried Residue of $CHCl_3$-Soluble Portion: Wt. G.	Color	Color of KOH Solution
A	1	"P"-A[2]	2	Small amt.	0.1833	Light reddish	Purple-red
	2	"P"-A	3.3	Small amt.	0.1906	Reddish	Purple-red
	3	"P"-A	4.6	Small amt.	0.1890	Reddish	Purple-red
	4	"P"-A	8.9	Small amt.	0.1876	Reddish	Purple-red
	5	"P"-A	7.9	Small amt.	0.1900	Reddish	Purple-red
B	6	"P"-B	3.3	Small amt.	0.1442	White	Purple-red
	7	"P"-B[3]	7	Small amt.	0.1482	White	Purple-red
	8	"P"-B	10	Small amt.	0.1440	White	Purple-red

[1] Experiments carried out at room temperature.

[2] "P"-A—Solution containing 0.1000 g. phenolphthalein + 0.4 g. KOH per 10 cc.

[3] "P"-B—Solution containing 0 1000 g. phenolphthalein + 0.12 g. KOH per 10 cc.

From these experiments it was inferred that variations in concentration of iodine did not appreciably affect the substitution reaction, but did have some effect on the amount of oxidation products.

SERIES II. VARYING TEMPERATURE—In the next series of experiments conditions relative to alkalinity, quantity of phenolphthalein, and iodine addition were kept nearly constant. As shown in detail in Table II, the reaction was carried out at room temperature, low temperature (2° to 5°), and at 50° and above by heating on the steam bath. Determinations of chloroform-soluble material were made as before.

TABLE II—EFFECT OF TEMPERATURE VARIATION

		Phenolphthalein Solution 10 cc.	Temperature of Solution °C.	10 Per cent Iodine Soln. Used Cc.	$CHCl_3$-Insol. Portion	$CHCl_3$-Sol. Portion, Dried Residue: Weight G.	Color	Color of KOH Soln.
C	1	"P"-C[1]	Room	8	Very little	0.2127	Reddish	Purple
	2	"P"-C	Ice	8	Very little	0.1977	White	Purple
	3	"P"-C	50	8	Consid. dark brown	0.1876	Red	Purple
	4	"P"-C	75	8	Consid. dark brown	0.1460	Red-brown	Purple
D	5	"P"-D[1]	Ice	8	Almost nil	0.2536	Reddish	Quite blue
	6	"P"-D	75–80	8	Consid. dark brown	0.1640	Brown	Purple

[1] "P"-C and "P"-D were both solutions containing 0.1000 g. phenolphthalein and 0.4 g. KOH per 10 cc.

The following observations were made: The residues from the chloroform extract were colored yellow when carried out at room temperature (Expt. C-1), very dark brown when at 50° and above (Expts. C-3 and 4 and D-5), and only very slightly yellowish or cream colored when solutions were previously cooled (Expts. C-2 and D-5). The potassium hydroxide solution of the chloroform-soluble residue indicated the presence of unsubstituted phenolphthalein in practically every case.

It becomes obvious from the results in Table II that elevation of temperature had a marked effect on the quantity of oxidation products, and, contrariwise, that the maintenance of low temperature (Expts. C-2 and D-5) resulted in the minimum amount of oxidation.

TABLE III—EFFECT OF VARIATION IN ALKALINITY

	Phenolphthalein Solution 10 cc.	10 Per cent Iodine Soln. Used Cc.	30 Per cent KOH Soln. Added Cc.	$CHCl_3$-Soluble Residue: Wt. Res.	Appearance	Color of Soln. of Residue
1	"P"-E[1]	5	0	0.1592	Pink	Purplish red
2	"P"-E	5	0.1	0.1986	Red	Red-purple
3	"P"-E	5	0.2	0.2230	Brown	Blue-purple
4	"P"-E	5	0.3	0.2294	Brown	Blue
5	"P"-E	5	0.5	0.2322	Red-brown	Blue

[1] "P"-E was a solution containing 0.1000 g. phenolphthalein and 0.033 g. KOH per 10 cc.

SERIES III. VARYING ALKALI CONCENTRATION—From the general difference in yields of tetraiodophenolphthalein as evidenced between Sets A and B in Table I, and C-2 and D-5 in Table II, the inference was drawn that variation in alkalinity played an important part in the completeness of reaction. This inference is borne out by the results of Table III, where concentration of alkali was made the only variable factor.

CONCLUSIONS—From the above experimental data the following conclusions were drawn:

(1) Errors of oxidation are caused primarily by elevation of temperature and these errors could be practically eliminated by maintenance of low temperature throughout the reaction. At low temperature, concentration of iodine mattered little (excess of this reagent is assumed in each case).

(2) Alkalinity was the most important factor in the progress of substitution.

(3) The reaction in practically every case was incomplete, even under the most favorable conditions. One-tenth of a gram of phenolphthalein should theoretically yield 0.257 g. tetraiodophenolphthalein. No advantage was gained by increase in alkali concentration beyond a certain point, as this was obviously neutralized by the increased consumption of iodine, and as soon as the alkali had been thus consumed the medium was rendered non-solvent for phenolphthalein and the progress of the reaction was checked. The use of sodium bicarbonate and insoluble carbonates to take care of the hydriodic acid formed was found quite ineffective.

It was evident from the better quantitative results in Table III that an 85 to 90 per cent yield of tetraiodophenolphthalein by a single treatment of iodine was attainable. The obvious step therefore suggested itself—to *repeat*, rather than attempt to *maintain* the conditions favorable for substitution; that is, to redissolve with potassium hydroxide the precipitate resulting in the reaction. By repeating this process of alternate precipitation (using acid) and re-solution with potassium hydroxide while temperature precautions were taken and excess of iodine employed, the error due to incompleteness of reaction was eliminated.

SOLUBILITY OF TETRAIODOPHENOLPHTHALEIN

Some difficulty was experienced in the extraction of the tetraiodophenolphthalein, owing to its varying solubility in chloroform. Determination of its solubility disclosed the fact that this compound was voluminous in form and readily soluble in chloroform, when precipitated from a cold concentrated solution, whereas when precipitated from warm dilute solutions it was granular and difficultly soluble in chloroform. In aqueous suspension this voluminous form went over into the granular form on standing or on heating.

A rough estimation of its solubility, as precipitated from a cold alkaline solution, showed the saturated chloroform extract to contain about one gram to 50 cc. of chloroform. The use of a mixture of acetone and chloroform (1 : 3) was found to increase the solubility of this compound nearly 100 per cent and to retard the transformation to the granular form. This mixture was therefore adopted in the final procedure.

On the basis of the above experiments and conclusions, a process was developed for the determination of phenolphthalein as embodied in the method herein proposed.

PROPOSED METHOD

The phenolphthalein (not over 0.25 g.) is dissolved in a minimum amount of strong potassium hydroxide (about 30 per cent) and a little water, in a 100 cc. beaker. A piece of ice, about 15 to 20 g., is added. To this solution, when sufficiently cool, there is added a prepared iodine reagent.[1] Sufficient iodine should be used to insure an excess of this reagent. Theoretically, 0.25 g. of phenolphthalein will require about 8 cc. of 10 per cent iodine solution. Concentrated hydrochloric acid from a buret is added drop by drop to complete precipitation. If sufficient iodine has been added, the precipitate, as well as the supernatant liquid, will be brown, otherwise more iodine is added to insure a few cc. in excess, and strong potassium hydroxide solution added from a buret, drop by drop, with stirring to dissolve completely the precipitate and consume all the excess iodine. This solution should be colored blue or blue-purple. The process of reprecipitation with strong acid and re-solution with strong alkali is repeated three or four times with small amounts of the reagents. In the acid condition there should be a brown precipitate resembling a periodide, and the supernatant liquid should be colored brown by the excess of iodine. The alkaline solution should be clear blue or purple-blue and no precipitate should be present. The alkaline solution is transferred with washing to a 150 cc. or 200 cc. separatory funnel, and a small piece of ice is added to keep the solution cold. Five-tenths cc. of 15 per cent sodium sulfite solution is added, and the mixture is acidified with a few cc. of strong hydrochloric acid. From 50 to 75 cc. of acetone-chloroform mixture (1 : 3) are then added. On shaking the tetraiodophenolphthalein precipitate is dissolved in the chloroform-acetone mixture. When the layers have separated, the chloroform-acetone extract is drawn off into another separatory funnel, a few cc. of chloroform-acetone added to the first funnel and this also drawn off into the second funnel to effect as complete a transfer as possible. This chloroform-acetone extract is then washed with about 20 cc. of water and when the layers have separated is transferred to a weighed Erlenmeyer flask. Two more extractions are made, using 35 cc. chloroform-acetone each, washed as above, and added to the rest in the flask.[1] The total volume of chloroform-acetone extract is then evaporated on the steam bath (using air blast if available) to dryness. Great care should be taken to avoid mechanical losses in transfer and evaporation. Spattering on evaporation can be avoided by allowing the last 20 to 25 cc. of chloroform-acetone to evaporate below the boiling point, shutting off the steam bath for that purpose. Rotation of the flask in last stages of evaporation also helps to prevent bumping. The residue is dried in an oven at 100° C. for 20 min., cooled, and weighed. The weight of tetraiodophenolphthalein, multiplied by the factor 0.3871, gives the phenolphthalein content.

Table IV contains in tabulated form the results obtained by this method.

TABLE IV—RESULTS OBTAINED BY PROPOSED METHOD

No.	Weight Phenolphthalein Taken Grams	Weight Phenolphthalein Calc. from Tetraiodophenolphthalein Grams	Weight Tetraiodophenolphthalein Found Grams
1	0.2500	0.2485	0.6414[1]
2	0.0200	0.0201	0.0521
3	0.0500	0.0497	0.1284
4	0.0100	0.00995	0.0257
5	0.0250	0.02499	0.0646
6	0.1000	0.01005	0.0260
7	0.2500	0.2484	0.6416[1]
8	0.1000	0.0988	0.2550
9	0.0500	0.0498	0.1286
10	0.0250	0.0247	0.0637
11	0.0100	0.01003	0.0259
12	0.0100	0.0103	0.0266
13	0.0500	0.0494	0.1276
14	0.1000	0.0995	0.2570
15	0.2500	0.2499	0.6457
16	0.2500	0.2499	0.6457
17	0.0080	0.00797	0.0206
18	0.0200	0.0204	0.0526
19	0.0400	0.0401	0.1037
20	0.1200	0.1197	0.3093
21	0.1500	0.1488	0.3844
22	0.1800	0.1786	0.4614[1]
23	0.2500	0.2500	0.6460
24	0.5000	0.5010	1.2950

[1] Spattered slightly.

APPLICATION OF METHOD TO MEDICINAL PREPARATIONS

Phenolphthalein, for medicinal purposes, usually occurs on the market in the form of pills or compressed tablets, containing as excipients sugar, starch, a little talc, and frequently considerable proportions of chocolate. Some contain additional drugs such as alkaloids, laxative resins, etc.

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[1] Iodine reagent is prepared by dissolving iodine to a concentration of 10 per cent in a 15 per cent potassium iodide solution and discharging the free iodine with alkali.

[1] If an emulsion is formed in the first extraction, it will be found that on drawing off this emulsified layer into the second funnel there will usually result a further separation into two layers: an upper layer of emulsion and a lower layer of clear chloroform-acetone extract. This clear lower layer is drawn off into a third separatory funnel for washing. The subsequent extractions with chloroform-acetone are passed through the second funnel containing the small amount of emulsion, before washing as indicated above.

In the absence of substances which are in themselves, or on subsequent treatment with iodine and alkali form compounds extractable in chloroform-acetone, the proposed method may be applied directly.

Ten tablets are weighed, ground up in a mortar, and preferably passed through a sieve (No. 40 or 60). A weighed amount representing an integral number of tablets (not over 5) is treated in a small beaker with potassium hydroxide solution. When all the phenolphthalein has dissolved it is transferred to a 50 cc. volumetric flask, made up to volume, thoroughly mixed and filtered. An aliquot part representing one or two tablets is then pipetted into a beaker containing a piece of ice (15 to 20 g.) and the determination is made as described in the method.

If the tablets contain chloroform-extractable material, particularly in the case of chocolate, preliminary treatment of the sample will be necessary.

Table V—Application of Method to Medicinal Preparations

No.	Composition as Stated on Label	Amount Phenolphthalein per Tablet Declared Grains	Amount Phenolphthalein Found by Method Grains
I	Phenolphthalein Chocolate q. s.	1.5	1.428 1.42 1.42
II	Phenolphthalein Podophyllin, $^{1}/_{4}$ gr. Belladonna ext., $^{1}/_{8}$ gr. Strychnine sulfate, $^{1}/_{60}$ gr. Cascarin	2	2.02 2.02 2.03
III	Phenolphthalein Sugar, 5 gr.	1	0.97 0.973 0.97
IV	Phenolphthalein Chocolate q. s.	1.5	1.445 1.445
V	Phenolphthalein	3	2.909 2.907
VI	Phenolphthalein Strych. sulf., $^{1}/_{500}$ gr. Ext. belladonna, $^{1}/_{100}$ gr.	1	0.98 0.98
VII	Phenolphthalein	2	1.97 1.99
VIII	Phenolphthalein	0.5	0.477 0.478
IX	Phenolphthalein	1	1.003 0.99
X	Phenolphthalein Chocolate	Not declared (Patent preparation)	1.94
XI	Phenolphthalein Chocolate	0.5 (Nearly all chocolate)	0.454 0.464
XII	Phenolphthalein Aromatics Sugar, 5 gr.	1	0.989 0.986

Ten or fifteen tablets are ground up as indicated before, or grated, if they are nearly all chocolate, and an amount equaling two to five tablets is weighed into a thimble of a 100 cc. Soxhlet extraction apparatus, covered with cotton to prevent loss of sample by floating off, and extracted with petroleum ether (b. p. 30° to 60°) for about 2 hrs. on the steam bath. This removes the fat, etc., but no phenolphthalein, as the latter is practically insoluble in that medium. All of the petroleum ether extract and that drained from the thimble is discarded. The sample is then subjected to extraction in a similar manner with C. P. acetone for at least one hour. The acetone extract, including that drained from the thimble, is evaporated on the steam bath and thoroughly dried in an oven at 100° C. to remove all traces of acetone. The residue is then dissolved in alkali, transferred to a 50 cc. volumetric flask, made up to volume, mixed, and filtered through paper. An aliquot part of the filtrate representing one or two tablets is used for the determination.

A number of phenolphthalein preparations were purchased in the open market and examined as indicated above, with the results shown in Table V.

SUMMARY

I—The behavior of phenolphthalein with iodine has been studied and facts deduced relative to: (1) its susceptibility to oxidation, (2) the conditions governing the formation of tetraiodophenolphthalein, and (3) the physical properties of the latter.

II—A method has been devised for the accurate quantitative determination of phenolphthalein with a special adaptation to its medicinal preparations. This method is based on the quantitative yield of tetraiodophenolphthalein, when a solution containing phenolphthalein and iodine is alternately made alkaline to complete solution, and acid to complete precipitation, at a low temperature. The tetraiodophenolphthalein is determined by extraction with acetone-chloroform mixture, applying the usual method of immiscible solvents.

THE COLORIMETRIC ESTIMATION OF ADRENALIN[1]

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With oxidizing agents and with alkalies adrenalin (or epinephrin) produces colors, usually intense, which vary from an orange to a red or brown or from a violet to a red. Under definite conditions the intensity of the color is proportional to the amount of adrenalin present, and methods have therefore been recommended for the quantitative estimation of this base in suprarenal glands by color processes.

The coloration with alkalies is slow in appearing, is modified by the presence of other organic matter, and has not proved satisfactory for quantitative work. With ferric chloride an intense green is produced, which fades quickly and is therefore not satisfactory for quantitative comparisons. With mercuric chloride an intense red is obtained which has been offered by Comesatti as a colorimetric method, but the color develops slowly and is easily changed by foreign substances. Potassium persulfate, potassium bichromate, iodine, potassium permanganate and potassium ferricyanide have at various times been tried with some success.

U. S. P. TEST

The U. S. Pharmacopeia adopted a modification of the permanganate test, using manganese dioxide for producing the color. This process, as applied to the estimation of adrenalin in dried suprarenal glands, consists in macerating 0.01 g. of the powdered glands in 10 cc. of distilled water containing 0.005 g. of manganese dioxide for one hour, filtering, and comparing the filtrate colorimetrically with prescribed mixtures of cobalt chloride and gold chloride solutions which correspond to 0.2, 0.4, 0.6, and 0.8 per cent of adrenalin, respectively.

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[1] Read at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

The color produced is a brownish orange, and since the red shade intensifies more than the yellow with increasing amounts of adrenalin it is necessary to vary the proportions of the two chloride solutions as well as their dilutions in order to match the colors. This shows that the color of the oxidized adrenalin and that of the mixed chloride solutions are not identical, although close enough for approximate matching.

EFFECT OF TEMPERATURE—No definite temperature is prescribed for the test, although in an oxidation process the temperature may be expected to have an influence. That it is an important factor is shown by tests on a solution of pure adrenalin at temperatures at 15°, 25°, 38°, and about 80° C. The color produced in an hour at 38° C. was decidedly the most intense. By comparison in a Duboscq colorimeter the color produced at 15° was 57 per cent as strong, and that at 25° C. 83 per cent as strong. At 80° C. the color was not comparable, the red shade having disappeared, leaving a dirty brown solution which would not compare with the others in any dilution. Since the color produced is compared with solutions of mineral salts not affected by ordinary changes in temperature, it is obvious that an error up to 40 per cent can be made by this factor alone.

EFFECT OF ACIDITY—The Pharmacopeia applies this test to dried suprarenal glands only, but adrenalin is used far more than the glands in medical practice, because it is definite in strength and activity. Since adrenalin is extremely sensitive both to alkalies and to oxidizing agents, it is necessary to insure against change by making its solutions sufficiently acid at least to neutralize the alkali dissolved from the glass in which it is stored, and either to replace the air with an inert gas or to add a reducing agent to the solution. Thus commercial solutions always contain an excess of acid, and many of them a reducing agent also. It is therefore desirable to learn what influence these agents might have on the color in the test.

The tests were accordingly repeated, using solutions containing 0.09 per cent of hydrochloric acid. This materially changed the color; the red tint appeared quickly but faded rapidly and the solution became brown. As nearly as could be ascertained by comparing colors of very different tints, the acid solution at 15° C. was about 30 per cent as strong as the neutral solution at 38° C., the acid at 25° about 60 per cent as strong, and at 80° C. about 50 per cent as strong. Slight amounts of mineral acid therefore change not only the intensity but the shade of color, and the change is more pronounced at 15° than at 25° or 38°. When 0.1 per cent of sodium bisulfite was added, the color was almost entirely destroyed.

It follows therefore that the U. S. P. test is not reliable except under definite conditions of temperature, composition, and acidity, and the mineral solutions which are used as standards must be adjusted to such conditions. This the Pharmacopeia has not done.

HALE AND SEIDELL TEST

In 1908, Krauss[1] recommended potassium iodate as the oxidizing agent, and in 1911 Hale and Seidell[1] further developed this test in its application to suprarenal glands, by heating to the boiling point 0.01 g. with 5 cc. of 0.025 *N* hydrochloric acid and 5 cc. of 0.2 per cent solution of potassium iodate, and after 15 min. comparing with a mixture of 3 cc. of a 2 per cent solution of potassio-platinic chloride and 9 cc. of a 1.2 per cent solution of cobaltous chloride.

As in the manganese dioxide test, the color produced is a reddish orange, and the greater the adrenalin content the more intense is the red, so that varying mixtures of the two chlorides are needed for comparison.

On testing this process it was noted that the shades of color varied considerably with different samples of adrenalin solution. In some cases a violet tint instead of a reddish orange was obtained, making comparisons with the standard impossible. Furthermore the color produced on doubling the quantity of adrenalin did not correspond, when diluted one-half, to that of the quantity directed. In other words, the color varied both in intensity and shade with varying quantities of the adrenalin solution. Again if the solution was heated for a few moments at 100° C. the color was changed.

TEMPERATURE EFFECT—To determine the temperature effect tests were run for one hour at 15°, 25°, and 38° C. The color was most intense at 38° C.; at 15° it was 45 per cent as deep, and at 25° it was 80 per cent, in neutral solution. In acid solution (about 0.015 per cent of hydrochloric acid) it was 55 per cent at 15°, 96 per cent at 25°, and but 30 per cent at 100° C. Thus acid promotes the development of this color at temperatures below 38° C. and fades it at high temperatures. It is therefore better to operate this test, with acid solutions, at a moderate than at a boiling temperature.

EFFECT OF ACIDITY—On increasing the amount of acid a pronounced red-violet was obtained which is very different from the reddish orange of the Hale-Seidell test. This accounted for the violet tint in some of the tests first made. The orange tint disappeared when as little as 0.015 per cent of hydrochloric acid was present. When 0.075 per cent of acid was present the purplish tint was less pronounced, and when 0.15 per cent was present the color was red-violet.

Further trials disclosed that the greatest intensity of color is reached in about 10 min. at 38° C., and further heating at this temperature for an hour makes no appreciable difference. The presence of sodium bisulfite in the solution diminishes the color in proportion to the amount of bisulfite present. When the adrenalin solution (1 : 1000) contained a like amount of sodium bisulfite (0.1 per cent) the color was reduced 10 per cent.

COLOR STANDARDS

In attempting to match the color (produced in acid solution) with a mineral solution, it was found that an ammoniacal solution of cobaltous chloride matches closely in certain depths.

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[1] *Apoth.-Ztg.*, **23**, 701.

[1] *Am. J. Pharm.*, **83**, 557.

AMMONIACAL COBALTOUS CHLORIDE—A solution made by dissolving 0.25 g. of cobaltous chloride ($CoCl_2.6H_2O$) in 10 cc. of water, adding a solution of 2 g. of ammonium carbonate (U. S. P. in translucent crystals) in 80 cc. of water, and making the solution up to 100 cc., matches the adrenalin color very closely in depths of 25 to 35 mm. (in a Duboscq colorimeter) but shades more to the red in deeper columns and to the blue in shallower. The ammoniacal cobalt chloride solution therefore differs enough in color to limit its usefulness, but can be used to verify the claim for a 1 : 1000 solution of adrenalin, provided the test be applied with proper precautions.

PURE ADRENALIN—A better standard is pure adrenalin. This can easily be obtained in pure form, and is permanent in this condition. The following method is recommended for standardizing solutions of adrenalin:

Dissolve 0.050 g. of pure adrenalin in 0.5 cc. of *N* hydrochloric acid and add water to make 50 cc. of solution (in a volumetric flask). If the solution to be compared contains bisulfite, 0.050 g. of C. P. sodium bisulfite should be added to this standard solution.

To 20 cc. of distilled water contained in a small (30 to 50 cc.) flask add 5 cc. of a 1 per cent solution of potassium iodate and 0.25 cc. of *N* hydrochloric acid. Warm to 38° C., add 0.5 cc. of the standard adrenalin solution, and continue the heat for 15 min. At the same time an acid solution of the iodate is prepared in the same way, warmed, and 0.5 cc. of the solution (1 : 1000) to be tested is added—or an equivalent quantity of a weaker solution. After 15 min. at approximately 38° C. cool the solutions and compare the colors in a colorimeter.

If the solution which is being standardized is within 20 or 25 per cent of the standard, comparisons are easily made. If it differs more than 25 per cent it is better to repeat the test, using more or less of the solution, so that the colors will not vary greatly.

It may also be compared with the standard ammoniacal cobalt solution, prepared as above, but here it is more necessary to have the two solutions in close relationship with each other, and to compare columns of 25 to 30 mm. in depth. If the adrenalin solution contains bisulfite it will read low on this account.

For estimating adrenalin in dried glands, digest 0.100 g. of the gland, for half an hour at 38° C., in 20 cc. of distilled water to which have been added 5 cc. of the iodate solution and 0.25 cc. of *N* hydrochloric acid, filter, and compare with the test made at the same time in the standard adrenalin solution. If the gland solution differs more than 25 per cent from the standard, an estimate can be made of its strength from which a second test can be made, using enough more or less of the gland to contain about 0.0005 g. of adrenalin. In this test the standard adrenalin solution should contain no bisulfite, and in all cases the standard adrenalin solution should be freshly prepared.

CONCLUSION

The above method had been compared repeatedly with the biological test, and has been found to give very satisfactory results. Doubtless the biological method will hold its place as the most reliable method for standardizing suprarenal glands or solutions of adrenalin, but the colorimetric test, when applied to preparations of known acidity and with an allowance, if necessary, for the presence of bisulfite, will be found sufficiently reliable.

A NEW METHOD FOR THE DETERMINATION OF PHENOL IN THE PRESENCE OF CERTAIN OTHER PHENOLS

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The few existing methods for the determination of phenol in the presence of other phenols are so tedious and so restricted in application that analysis of materials regarding which information is much desired is often out of the question. The method here presented is a colorimetric one, approaching the average of such methods in applicability, convenience, and accuracy. In addition to its far wider range of application, it appears to offer advantages over existing methods in many cases where these are suitable. It is based on the fact that under certain conditions Millon's reagent yields a red color with phenol but not with certain other phenols.

Millon's reagent has been much used as a general reagent for phenolic hydroxyl, ordinarily in dilute solution and with heat. Elvove[1] employed it for determining either phenol or cresol singly present as preservative in serums, adding it in unprecedentedly high concentration merely to avoid the necessity of heating. He noted that the colors yielded by phenol and cresol differed in rate of development and in final intensity, and found, moreover, that different samples of commercial cresol were not always closely comparable. In a comparison of equimolecular solutions of phenol and the three pure cresols made by the present author, the marked differences in tint, maximum intensity, rate of development, and rate of fading led to running a similar series of tests in a boiling water bath to expedite and extend the reaction. Under these conditions the red color yielded by phenol became much intensified and nearly permanent, whereas the red colors first yielded by the cresols soon gave place to various shades of yellow. The combination of high concentration and heat thus makes the reagent available for distinguishing between phenol and certain of its homologs.

EXPERIMENTAL

PREPARATION OF REAGENT—The Millon reagent must be prepared in precise accordance with directions, in which connection the observations of Elvove were found sound and valuable. An excessive proportion of free nitric acid will bleach the color afforded by phenol, while in the presence of insufficient acid the red color given by the cresols, especially *o*-cresol, is discharged with inconvenient slowness. To 2 cc. of mercury, best measured from a small buret, in a 100 cc. Erlenmeyer flask, are added 20 cc. of C. P. concentrated nitric acid, and the flask is placed under a hood at room temperature until the mercury is dissolved—about 15 min. The solution is diluted with 35 cc. of water, and if basic salt separates, nitric acid is added by drops until all is dissolved. Caustic soda (10 per cent) is next slowly added by drops with thorough mixing until the somewhat curdy precipitate first formed no longer redissolves but disperses to an evidently permanent turbidity. Then are added exactly 5 cc. of dilute nitric acid containing 0.2 of its volume of C. P. concentrated nitric acid, and the solution is well mixed. Preparations thus made act very uniformly, but the same one should preferably be used upon sample and standard. The solution remains fit for use throughout an entire working day but probably should not be used the second day.

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[1] U. S. Public Health Service, Hygienic Laboratory, *Bull.* **110** (1917), 25.

DETAILS OF METHOD—In making a test 4 mg. of the phenol or mixture of phenols in nearly neutral aqueous solution are placed in a 20 mm. test tube, which for subsequent convenience is best provided with a graduation mark at 25 cc., and diluted to 6 cc. Five cc.[1] of the Millon reagent is flowed over the inside of the tube, the contents well mixed, and the tube placed in a water bath previously brought to boiling and maintained at boiling for exactly 30 min.,[2] then transferred to a bath of cold water in which it remains 10 min. The contents are next acidified with 5 cc. of dilute nitric acid, containing 0.2 of its volume of C. P. concentrated nitric acid free from oxides of nitrogen,[3] and after brief mixing brought up to a total volume of 25 cc. with water and thoroughly mixed. The resulting solutions appear to undergo no appreciable changes in color for many hours. If phenol only is present the solution is perfectly clear. Most other phenols yield sediments, comparable in color to the solutions, which may be removed by filtration after standing about 10 min. Neither the sediments nor filter paper appear to absorb any appreciable trace of the red color yielded by phenol. Table I gives the results obtained by thus testing various phenolic bodies.

The results given in this table are sufficient to show that the proposed test for distinguishing phenol from certain other phenols is of wide application. It is doubtful if the true color yielded by any of the higher phenols on the list is characterized by even a trace of orange, for contamination by phenol or a derivative is difficult to exclude. Such contamination of course existed in the tar acids from the various creosotes and was likewise proved by fractional distillation to be present in the specimens of *o*-cresol and guaiacol employed. The effect produced by the addition of formaldehyde will be discussed later.

Excluding salicylic acid and β-naphthol which obviously invalidate the test by their presence, *m*-cresol was found to exert the greatest masking effect upon phenol. In pure solution 0.005 mg. of the latter substance affords a faint orange; 0.01 mg. a decided orange. In the presence of 4 mg. *m*-cresol the effect of 0.01 mg. phenol is merely to render the yellow color somewhat deeper and richer; 0.02 mg. much intensifies the effect, while 0.04 mg. brings in a distinctly orange tint.

TABLE I—COLORS FROM PHENOLS BY MILLON'S REAGENT AFTER HEATING

PHENOL	COLOR OF SOLUTION	COLOR AFTER ADDING FORMALDEHYDE
Phenol	Deep red	Strong yellow
o-Cresol	Faintly orange	Greenish yellow
m-Cresol	Strong yellow	Very slightly paler
p-Cresol	Greenish yellow	No change
o-Xylenol	Faintly orange	Greenish yellow
p-Xylenol	Greenish yellow	No change
Thymol	Faint greenish yellow	No change
Resorcinol	Greenish yellow	No change
Pyrogallol	Colorless	No change
Guaiacol	Faintly orange	Greenish yellow
α-Naphthol	Greenish yellow	No change
β-Naphthol	Strong brown	No change
Salicylic acid	Deep red	Strong yellow
o-Cresotic acid	Faintly orange	Colorless
Beechwood creosote, redistilled:		
Fraction, 202°	Strong red	....
Fraction, 202°–208°	Moderately orange	Greenish yellow
Fraction, 208°–216°	Very faintly orange	....
Fraction, 216°–230°	Greenish yellow	....
Residue	Faintly greenish yellow	....
Tar acids from gas-tar creosote, redistilled:		
Fraction, 202°	Strongly red	....
Fraction, 202°–211°	Slightly orange	Yellow
Fraction, 211°–225°	Yellow	....
Residue	Greenish yellow	....
Residue from 1st distillation	Very faintly brown	....
Tar acids from blast-furnace creosote, redistilled:		
Fraction, 210°	Strongly orange	Yellow
Fraction, 210°–225°	Slightly orange	....
Fraction, 225°–255°	Yellow	....
Residue	Slight yellow	....
Residue from 1st distillation	Faintly yellow	....

QUANTITATIVE MEASUREMENTS

In the progress of the work three possible methods for quantitative measurement were developed.

METHOD I—Inasmuch as failure at first followed efforts to separate the red and yellow colors, either by chemical or physical means, it appeared necessary to make quantitative measurement of the red in presence of the yellow. Standard tubes were therefore made up from mixtures of phenol with synthetic "tricresol" prepared from the C. P. isomers, the total phenols present in each case amounting to 4 mg. As in the sample tubes, all were made up to 25 cc. and filtered, and 20 cc. portions of the filtrates were compared in 50 cc., tall form, Nessler tubes. Since commercial cresols may differ widely in the relative proportions of the various isomers present, and since the various isomers yield various tints and intensities of yellow, some judgment is necessary in selecting a proper composition for the synthetic tricresol, particularly if small percentages of phenol are to be determined.

METHOD II—To avoid the uncertainties involved in the use of a standard tricresol it was decided to add a known proportion of phenol to a portion of the sample itself, and to compare the color afforded by this mixture as a standard with that afforded by the original sample. Such a method obviously demands the use of an appropriate colorimeter. The only one at hand was the standard Duboscq instrument.

Inasmuch as a colorimeter appears never to have been employed in such a manner it is necessary to subject the proposition to mathematical analysis.

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[1] The strongly corrosive liquid should not be drawn into a pipet by mouth suction.

[2] After 15 min.' boiling the original red color from other phenols may not be entirely discharged nor will the color from phenol have been fully developed. After 45 min.' boiling the color from phenol shows progressively diminishing intensity.

[3] Blown with air till colorless, if necessary.

Let a portion of pure phenol solution of P concentration be raised by further addition to $(P + p)$ concentration and the colors of the two solutions be developed and matched in a colorimeter, setting the original solution at S and determining R as the reading of the stronger. Then the equation of condition will be

$$PS = (P + p)R, \text{ and } P = \frac{pR}{S - R}.$$

Now any error (e) in the reading R will produce an error (E) in the determined concentration P, according to the equation

$$P + EP = \frac{p(R + eR)}{S - (R + eR)}, \text{ and } E = \frac{eS}{S - R(1 + e)}.$$

The value of E will evidently depend largely upon the ratio R:S, which may be represented by ρ; or $R = \rho S$. Then

$$E = \frac{e}{1 - \rho(1 + e)},$$

which may be solved for various values of e and ρ as given in Table II.

TABLE II—ERRORS IN DETERMINED CONCENTRATION FROM ERRORS IN READING

$$E = \frac{e}{1 - \rho(1 + e)}$$

	$(e = 0.01)$	$(e = 0.02)$	$(e = 0.04)$
ρ	E	E	E
0.5	0.020	0.041	0.083
0.6	0.025	0.052	0.106
0.7	0.034	0.070	0.147
0.8	0.052	0.109	0.238
0.9	0.110	0.244	0.625

Evidently the ratio R:S must be kept as low as possible without rendering the colors difficult to match. When p approaches 0.5 P the theoretical and practical requirements will be most nearly satisfied.

If, instead of starting as above with a pure solution of phenol, we start with a mixture which also contains cresol in concentration C, the relative intensity of the color of cresol as compared to phenol being I, the equation of condition for balancing the colors in the colorimeter becomes:

$$PS + ICS = (P + p)R + ICR$$

No further advance can be made until the value of I is determined by experimentally solving

$$I = \frac{(P + p)R - PS}{C(S - R)}.$$

The experimental values were obtained on quantities of 2 to 4 mg. of the cresols, the quantity being limited by the formation of precipitates. To one tube of each pair was added 0.04 mg. phenol; to the other 0.06 to 0.08 mg. The values thus obtained for I were: *m*-cresol, 0.009; *p*-cresol, 0.005; *o*-xylenol, 0.008; *o*-cresol, somewhat lower than *p*-cresol, as nearly as could be determined on a somewhat impure substance. Inasmuch as *m*-cresol clearly yields a heavier color than any of the other phenols listed in Table I, and since both *o*-cresol and *p*-cresol must necessarily accompany phenol if the latter is present in *m*-cresol it is fair to take the mean value for I as 0.007. Substituting in the equation of condition we get, therefore:

$$P = \frac{pR}{S - R} - 0.007\ C$$

The value of C cannot, of course, be known until P is determined, but for all practical applications of the formula it may be approximated closely enough by subtracting the value of $\frac{pR}{S - R}$ from the concentration of total phenols, T. The precise value of P can be derived from the formula

$$P = \frac{1}{1 - I}\left(\frac{pR}{S - R} - IT\right).$$

To carry out this method dilute the sample until it contains 0.1 per cent total phenols in nearly neutral aqueous solution. Measure 4 cc. into each of two test tubes and add to one about one-half the quantity of phenol believed to be already present. Add water to both tubes to bring total volume to 6 cc., then Millon's reagent, and proceed as already described until both tubes have been made up to the final volume of 25 cc. After standing at least 10 min. to allow sediment to form, both are filtered shortly before being compared in the colorimeter, the filtrates being repassed through the papers until perfectly clear. Fill the two filtrates into the colorimeter cups, and make the setting on the sample at a point on the scale appropriate for the intensity of the color. In making the reading it is to be remembered that intensities of color, not hues, are being matched. A difference in hues naturally becomes conspicuous when low percentages of phenol are being determined or when there is too much difference between the phenol contents of sample and standard. The proper point is best arrived at by moving the plunger back and forth by it several times until the eye becomes assured where it lies. After taking several readings the liquids are reversed in the apparatus and readings taken on the other scale. Whether the cups themselves may be reversed along with the liquids depends on whether they are positively known to be exactly similar. The final figure will be the average of the averages of the two series, and the percentage of phenol can be calculated by the above formula.

The highly corrosive liquids must be kept from contact with the metal fittings of the colorimeter, including the cups.

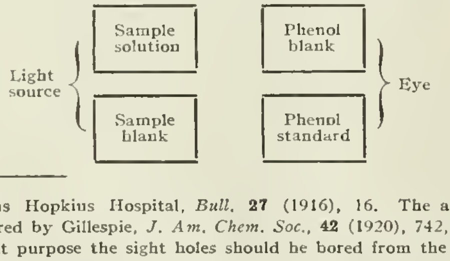
METHOD III—In further investigations it was discovered that the red color is more sensitive than the yellow to the action of certain reducing agents, and that by proper treatment the red may be bleached or, more correctly, reduced to yellow, without marked effect upon the yellow originally present. The last column of Table I gives the results obtained when 0.1 cc. of commercial 37 per cent formaldehyde solution was added and the tests left over night. That the tints originally afforded by certain higher phenols became slightly modified by formaldehyde is believed to be due chiefly to contamination by phenol or a derivative: first, because the presence of phenol was demonstrated by fractional distillation in the cases of *o*-cresol and guaiacol; and second, because parallel tests on *m*-cresol with 0.05 to 0.2 cc. of formaldehyde showed identical tints, indicating that the true color of *m*-cresol was not being measurably affected.

The first steps of the method are the same as in the previous ones except that two tubes of the sample must be run. After acidification both tubes are made up to 25 cc. but to the tube intended for the blank there are first added 3 cc. of dilute formaldehyde containing 0.02 of its volume of the commercial 37 per cent product. Both tubes are stoppered, well mixed, and left over night. At the same time two standard tubes of phenol are run, each containing 0.8 mg. (4 cc. of a 0.02 per cent solution). After acidification one tube is made up to volume with water only, the other with water and 3 cc. of the dilute formaldehyde like the blank, thus constituting a blank of the second order, which will be termed hereafter the "phenol blank." Further execution of the method is possible by two modifications.

Modification A—Into a 50 cc. Nessler tube, tall form, are pipetted 20 cc., 10 cc., or 5 cc. of the sample solution, depending upon the depth of the red color, and the same amount of the sample blank is pipetted into a similar tube. If the pipetting is carefully done, filtration is usually unnecessary. The phenol standard and the phenol blank are each poured into 25 cc. burets. A small portion of the phenol standard is now run into the sample blank, and the same quantity of the phenol blank into the sample solution, both are well mixed, and the colors compared. Continue with the titrations until the colors match. If excess of standard phenol is inadvertently added a back titration for correction may be made on the tubes reversed. It is imperative to carry through the whole titration once started without delay, for formaldehyde remaining in the blanks will soon cause fading of the red added. Each cc. of the phenol standard used in the titration is equivalent to percentages of phenol in the various sized portions of the sample solution used as follows:

20 cc. sample solution, 1 per cent
10 cc. sample solution, 2 per cent
5 cc. sample solution, 4 per cent

Modification B—The variation here consists in the use of a comparator, similar to that described by Hurwitz, Meyer and Ostenberg.[1] The instrument demands a supply of matched test tubes, *i. e.*, tubes of uniform quality and thickness of glass, in which equal volumes of liquid stand at equal heights, since observations are made by light transmitted horizontally. Sufficient quantities of the solutions are decanted into the tubes, or filtered, if necessary, and the tubes are arranged in the comparator as shown below.[2]



Final observations may be checked by reversing the block, or reversing the members of one series.

The primary phenol standard and phenol blank as prepared and used in this modification are equivalent to 20 per cent phenol in the sample. From the primary standard and blank all other standards and blanks necessary are made by appropriate dilution with a special nitric acid solution containing 0.2 of its volume of the dilute nitric acid already prepared. If the phenol content of the sample proves greater than 20 per cent, both sample solution and sample blank will be parallelly diluted with the special nitric acid until a match is obtained.

APPLICATION OF METHODS—In order to test the methods five synthetic samples were prepared by an assistant to be run as "unknowns." It later developed that the *o*-cresol contained, as nearly as could be determined, 0.9 per cent of phenol. Making the necessary corrections therefor the results obtained are given in Table III.

It will be noted that Method III affords consistently low results. The use of secondary phenol standards prepared by dilution of a primary standard is not responsible, for such secondary standards in fact tend to be slightly paler than equivalent primary standards directly prepared. The cause must lie in a slight bleaching of the cresol colors, particularly of *m*- and *p*-cresol, effected by formaldehyde, too slight to be detected on direct observation of the pure colors to which the eye is far less sensitive than to tints of red. Large amounts of formaldehyde in fact effect marked bleaching of the yellow.

In scrutinizing the claims of the various methods for practical use it is obvious that all may be expected to afford useful results on percentages of phenol above a minimum of one per cent of the total phenols present. The most delicate readings for minimal percentages are naturally afforded by Modification A of Method III. No experiments on high percentages are cited for it is obvious that the errors arising from the colors yielded by other phenols become decreasingly important factors as the relative proportion of phenol increases. It is probable that Method III will be found most widely useful despite the somewhat low results it affords.[1] Modification B is particularly applicable when the work is of considerable bulk. A single set of standards, once prepared, will serve for

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[1] Johns Hopkins Hospital, *Bull.* **27** (1916), 16. The apparatus is well pictured by Gillespie, *J. Am. Chem. Soc.*, **42** (1920), 742, though for the present purpose the sight holes should be bored from the other sides of the block in order to include but two tubes in each series. Cooledge, THIS JOURNAL, **12** (1920), 499, describes a more complicated but presumably more rapidly operated apparatus, not here tested.

[2] Compare Clark and Lubs, *J. Bact.*, **2** (1917), 109.

[1] In Method III the eye compares hues rather than intensities. Consequently partial bleaching of yellow in the blank means that correspondingly less red will be added to it in order to match the orange hue of the sample. Further experiments have indicated that in all ordinary mixtures the *p*-cresol will exert fully as great an effect as the *m*-cresol in depressing the apparent phenol content, while the effect of the *o*-cresol is probably negligible. It is believed that the following figures quite closely represent results which may be expected by Method III on samples of commercial cresol and which may serve as data for corrections:

Phenol, as percentage of total phenols	Percentage recovery by Method III
Less than 5	75
At 5	80
At 10	85
At 20 (4 mg. sample)	90
At 20 (1 mg.)	95
Above 20 (1 mg.)	100

The above figures were obtained on mixtures prepared as if from synthetic tricresol (35 : 40 : 25) but lacking the *o*-cresol, since this substance could not be obtained absolutely free from phenol.

Table III—Determination of Phenol in Synthetic Samples

Sample No.	Per cent Composition o-Cresol	m-Cresol	p-Cresol	Phenol	Method I[1]	Method II p = 1%	p = 2.5%	Method III Modif. A	Modif. B
1	34.7	40	24	1.3	1.4	1.46 1.41	1.22	1.0	1.0
2	59.5	25	10	5.5	6.0	5.12	5.11 5.54	4.75	5.0
3	37.8	10	50	2.2	2.1	1.92 2.20	2.17	1.65	1.75
4	39.6	17.5	40	2.9	3.0	2.72	2.77 2.54	2.25	2.25
5	19.8	40	36	4.2	3.9	3.81	4.02 3.97	3.0	3.0

[1] Standard tricresol = 35 *o*-cresol : 40 *m*-cresol : 25 *p*-cresol.

as many samples as can be handled during a whole working day. Moreover, if the comparator is constructed to take the 20 mm. test tubes used for developing the color, and these are matched up for size, etc., before use, transference of liquids from one container to another may be much reduced. The proportions of sample, reagent, etc., recommended developed somewhat spontaneously in the course of the work. There is possibly no reason why, if preferred, the total amount of phenols may not be increased to 5 mg. in a volume ranging from 5 to 8 cc.

The color characterizing phenol is not greatly different from the color of solutions of cobalt nitrate, so that the preparation of a set of permanent standards may be possible.

Most of the mercury may be conveniently recovered by treating accumulated residues with an excess of formaldehyde and, after a few days' standing, warming on the steam bath until the metal has collected in coherent liquid form.

In applying the method to the determination of phenol in commercial products preliminary purification will often be necessary. Alcohol should not be present in more than traces for it becomes converted to acetaldehyde which can bleach the color. "Saponified cresol solutions," practically free from tar oils, whether containing fatty oil soaps or rosin soaps, may be run by the regular method, though the soap is preferably first removed by precipitation with barium nitrate. The determination of phenol in coal-tar creosote or in products manufactured therefrom naturally will be of interest only in connection with a determination of the total phenols or "tar acids." All existing practical methods for determining the latter measure the volume of total phenols after solution in aqueous alkali or in a solvent oil. In either case it will be a simple matter afterward to bring the phenols into aqueous alkaline solution, extract and steam out the oils, dilute, neutralize, make to appropriate volume, and filter. Distillation with steam may be necessary in the case of some materials.

SUMMARY

A colorimetric method of fair accuracy is described for the determination of phenol in presence of certain other phenols, both monohydric and polyhydric, based on the red color yielded by Millon's reagent under certain conditions with phenol, but not with these other phenols. The method can determine a minimum approaching 0.04 mg. of phenol in the presence of 4 mg. of cresol, etc., in a volume of 4 cc. and is applicable to a variety of commercial products after simple preliminary treatment.

THE ELECTROMETRIC ANALYSIS OF ARSENICALS[1]

By Charles S. Robinson and O. B. Winter

Michigan Agricultural College Experiment Station,
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Received March 28, 1918

Trivalent arsenic in arsenicals is usually determined by titration with iodine in a solution made alkaline with sodium bicarbonate[2] using starch, or the color of the iodine itself, as the indicator; pentavalent arsenic, when present alone, is reduced to the trivalent form[3] and determined as above; and where both are present the pentavalent form comprises the difference between the amounts of As^{III} before and after the action of a reducing agent,[4] calculated as As^{V}. The reducing agents recommended are hydriodic acid and cuprous chloride.[5]

The above methods in some cases require certain time-consuming and inconvenient preparatory steps. Thus, when determining pentavalent arsenic in London purple the organic matter must be destroyed prior to the reduction of the As^{V},[6] or the arsenic distilled off as $AsCl_3$[7] in the presence of blood charcoal; and in the determination of As^{III}[8] in the same product the solution must be filtered in order to remove the colored suspended matter. Also the determination of As^{V} is an indirect one involving the intermediate step of reduction before the actual determination can be made.

The method described in the present article has been developed with the idea of obviating some of these difficulties. It is based upon the variation in oxidation potential[9] and its use in the present instance was suggested by the work of Crotogino.[10] The same principle has been used in a number of other cases, as for instance by Hildebrand[11] and by Forbes and Bartlett[12] for the titration of iron with potassium bichromate, and by Kelley and his coworkers for the determination of certain elements in steels.[13] Briefly, the method depends upon the fact that oxidation from the electrochemical standpoint means the addition of positive charges to the ions or the removal of negative charges while reduction is, of course, the reverse. A solution containing an oxidizing agent may be conceived as containing an excess of positive charges while a solution containing a reducing agent contains an excess of negative charges. If then in a cell arranged as follows:

Pt | Oxidizing agent | *N* KCl-calomel | Pt a reducing agent is added to the oxidizing material, a marked change occurs in the e. m. f. of the combination at the point where the reversal of sign occurs, *i. e.*, at the point where the oxidizer is completely reduced. The same holds true of course for the addition of a solution of an oxidizing agent to a solution of a reducing agent in a similar apparatus.

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[1] This work was done in the chemical laboratory of the Michigan Agricultural College Experiment Station and the results are published with the permission of the Director.

[2] *Assoc. Off. Agr. Chem.*, II, No. 1, p. 8 (17).

[3] *Ibid.*, p. 11 (32).

[4] *Ibid.*, p. 8 (19).

[5] *Ibid.*, p 6 (5); p. 8 (19).

[6] *Ibid.*, p. 8 (19).

[7] Report on Insecticides—1917. Read at the Annual Convention of the A. O. A. C. held in November 1917. Not yet published.

[8] *Assoc. Off. Agr. Chem.*, II, No. 1, p. 8 (17).

[9] For general discussion of this subject see Ostwald, "Allgemeine Chemie," 2nd. Ed., II, 883; Bancroft, *Z. phys. Chem.*, **10** (1892), 387; Neumann, *Ibid.*, **14** (1894), 193; Ochs, Inorg. Dissert., Basil, **1895**; Ostwald, *Z. phys. Chem.*, **15** (1894), 399; Peters, *Ibid.*, **26** (1898), 193; Bigelow, "Theoretical and Physical Chemistry," p. 484; or Nernst, "Theoretische Chemie," 7th Ed., p. 789.

[10] *Z. anorg. Chem.*, **24** (1900), 225.

[11] *J. Am. Chem. Soc.*, **35** (1913), 869.

[12] *Ibid.*, **35** (1913), 1527.

[13] *J. Am. Chem. Soc.*, **38** (1916), 341; This Journal, **9** (1917), 780; **10** (1918), 19; **8** (1916), 719.

In the work discussed in the present article the following chemical reaction is fundamental:

$$H_3AsO_3 + 2I + H_2O \rightleftharpoons H_3AsO_4 + 2HI \quad (1)$$

If the solution is alkaline with sodium bicarbonate so that the hydriodic acid is removed as fast as formed, the reaction proceeds to completion from left to right. If, however, the solution is acid, the reaction follows the opposite course. The former case is that of the titration of arsenious acid with standard iodine solution, while the latter applies to the titration of arsenic acid with hydriodic acid, *i. e.*, with an iodide in acid solution as hereinafter described. The use of this latter reaction for the estimation of As^{V} has not been utilized heretofore because of the lack of a suitable means of determining the end-point, though the chemical process involved has been the basis of its indirect determination as outlined above.

APPARATUS

The apparatus used in the present work was essentially the same as that described by Hildebrand,[1] excepting that a mechanical stirrer was added and a reflecting galvanometer of the box type was used in place of the capillary electrometer, a substitution which should prove very advantageous where any large amount of work is to be done. The arrangement of the various parts, with the exception of the stirrer, is shown in Fig. 1, where B is a source of electromotive force such as a storage or dry cell; *ab*, a slide wire bridge with the sliding contact *d;* V, a Weston millivoltmeter; R, a resistance to steady the galvanometer G; C, a calomel half-element which, with the platinum electrode E, dips into the beaker D in which the titration is made;[1] F, a support for the calomel half-element; and K, a key.

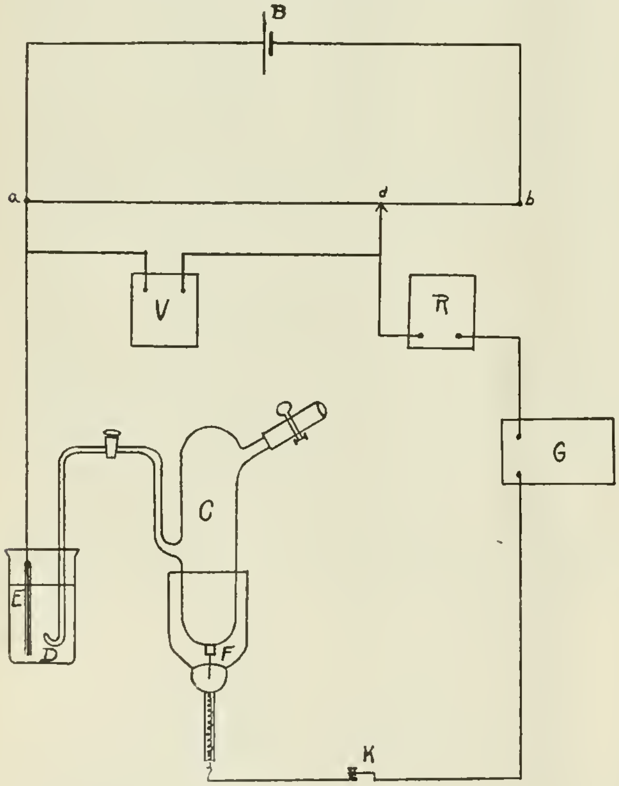

Fig. 1

The slide wire *ab* was improvised from a piece of manganin wire stretched on a stick, the sliding contact consisting of a test tube holder. The tip of the side arm of the calomel electrode and also that of the buret which was used in making the titrations were drawn down to a capillary and bent upwards to prevent the entrance into them of gas. The calomel electrode, of the ordinary type, was conveniently held in the support F, consisting of a piece of glass tubing of slightly larger diameter than the electrode. It was drawn down to form a mercury reservoir, in the bottom of which was sealed a short piece of platinum wire welded to a long piece of copper wire coiled into a spiral. To protect this spiral a short piece of glass tubing was sealed to the reservoir and its lower end plugged with paraffin or sealing wax. This support may be held permanently in a buret clamp and the calomel element removed and replaced with ease. Contact was made by the terminal wire of the half-element dipping into mercury in the reservoir of the support. In this way the wear on this wire is reduced to a minimum and the life of the cell prolonged indefinitely. As the copper wire from the bottom of the holder is broken off with usage it may be replaced by drawing more from the coil in the tube.

METHOD OF PROCEDURE

(1) DETERMINATION OF As^{III}—It may be well to state at the outset that under ordinary circumstances the electrometric titration of trivalent arsenic possesses no advantage over the ordinary method of titration using starch, or the color of the iodine itself, as the indicator. In some colored solutions, however, it may be of decided value.

The procedure for preparing the sample was essentially the same as that ordinarily employed for the titration of trivalent arsenic with iodine. A 4-g. sample was weighed out, dissolved in hydrochloric acid at a temperature of less than 60° C., transferred to a 500 cc. graduated flask, and made to volume. Twenty-five cc. aliquot parts were made alkaline with sodium bicarbonate and titrated with 0.1 *N* iodine. To show the course of the reaction several titrations were made by adding the iodine solution in small amounts and taking the readings of the millivoltmeter which corresponded to the amounts of iodine used. The following data which were obtained in one of these titrations on a sample of London purple may be considered as a typical example of the titration of an arsenious compound.

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[1] *Loc. cit.*

[1] An apparatus of the type described by Kelly, Adams and Wiley, This Journal, 9 (1917), 780, was not available for our investigations but it appears to be a very desirable instrument for a laboratory where the inspection of insecticides constitutes a considerable part of the work done.

TABLE I

Cc. 0.1 *N* I	Milli-volts	Cc. 0.1 *N* I	Milli-volts	Cc. 0.1 *N* I	Milli-volts	Cc. 0.1 *N* I	Milli-volts
0.0	190	5.0	180	7.6	200	8.6	300
1.0	180	6.0	180	7.8	200	8.8	315
2.0	180	7.0	195	8.0	200	9.0	320
3.0	180	7.2	195	8.2	200	9.5	325
4.0	180	7.4	200	8.4[1]	280	10.0	325

[1] End-point with iodine color as indicator.

These data are shown graphically in Fig. 2, the ordinates representing millivolts, and the abscissas cc. of 0.1 *N* iodine.

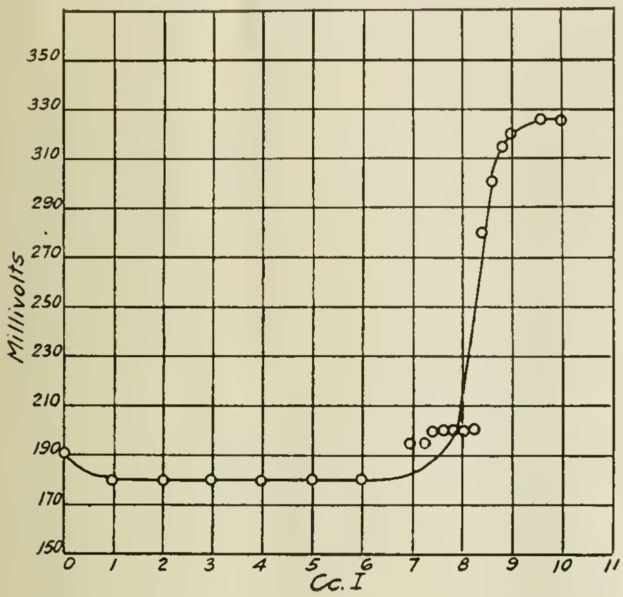

FIG. 2

Under ordinary circumstances this procedure is unnecessary. For practical purposes,[1] all but a few tenths of a cc. of the sample is run into the beaker from a buret, made alkaline with sodium bicarbonate, the sliding contact set so that the proper voltage[2] is indicated on the voltmeter, the stirrer started, and the iodine solution introduced at the usual rate as determined by the drainage of the buret. The completion of the oxidation is indicated by the change in the direction of the swing of the beam of light when the key is tapped or by its crossing the zero mark if the titration is carried out with the circuit closed. At this point the addition of iodine is stopped, the remainder of the aliquot of sample introduced, and the titration completed by the addition of iodine solution in sufficiently small increments to permit the accurate determination of the end-point.

Table II shows the results of several analyses made by this method and the corresponding results obtained by the usual method of titration.

TABLE II

MATERIAL	Per cent As_2O_3 Electrometric	Official
London purple A	15.95	15.90
London purple B	25.57	25.50
Arsenious acid	98.65	98.65
Zinc arsenite	64.59	64.59

(2) DETERMINATION OF AS^V—The titrimetric reversal of the above process is somewhat more complicated than the preceding operation and, as stated before, it must be carried out in an acid solution. In order that reduction may take place with sufficient rapidity, the acid concentration must be high and the solution hot. It appears that concentrated sulfuric acid must compose about 50 per cent by volume of the solution at the end of the titration, and that the temperature must approximate 90° C. If the temperature is much lower than this the reaction is slowed down, while if it rises higher some of the reducing agents (hydriodic acid and sulfur dioxide[1]) may escape. The gaseous nature of the reducing agents also makes it necessary to use the special buret mentioned above, *i. e.*, one with the tip drawn out to a capillary and bent upwards to form a hook at the end. This allows the solution to be introduced at the bottom of the beaker, from which point it must pass through the whole depth of the solution contained therein before reaching the air.

An efficient stirrer is a requisite for the success of the operation. While the agitation of the liquid may be done by hand, some form of mechanical stirrer is not only more efficient but far less tedious where a number of determinations are to be made.

The same method was followed in preparing the solution for determining pentavalent arsenic as was used for the trivalent form but in order to show the course of the reaction for As^V, a 2-g. sample of pure As_2O_3 was weighed out, oxidized with nitric acid, the latter replaced with sulfuric acid,[2] and the solution made to 500 cc. A 25 cc. aliquot part was used for the titration. This was transferred to a 100 cc., low-form beaker, sufficient concentrated sulfuric acid added to give about an equal volume of acid and water at the end of the titration, cooled to 90° to 95° C., and titrated

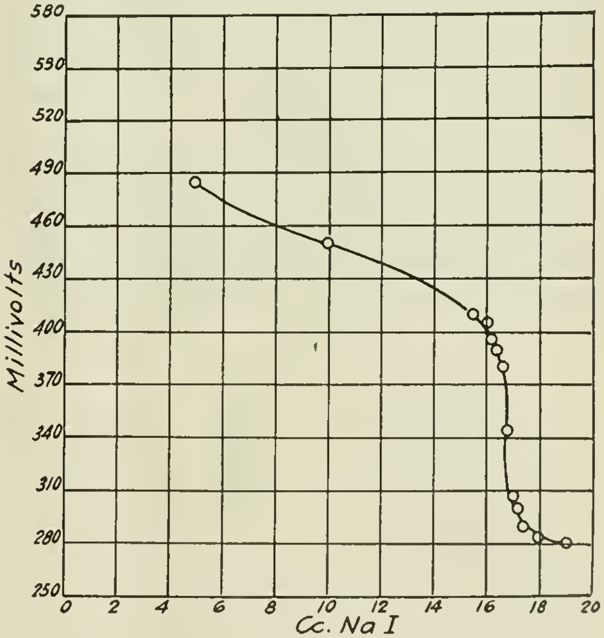

FIG. 3

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[1] With a little practice this step may be omitted and the whole sample titrated in one operation.

[2] The voltage of a solution in which the As_2O_3 is just oxidized may be determined by running several determinations by the graphical method on standard arsenious acid. This value in our work was about 260 mv.

[1] Hot concentrated sulfuric acid oxidizes hydriodic acid with the formation of iodine and sulfur dioxide, but as the latter is also effective in reducing pentavalent arsenic the final result is the same as though only hydriodic acid were present.

[2] The final solution must be entirely free from nitric acid or the end point will not be sharp.

with 0.1 *N* sodium iodide solution. The temperature was kept constant to within 5° by means of a low flame under the beaker. Table III gives the amounts of sodium iodide added, the corresponding readings of the millivoltmeter, and also a comparison of the amounts of As_2O_5 found in 500 cc. of the solution. The data are shown graphically in Fig. 3, where the ordinates represent millivolts, and the abscissas cc. of 0.1 *N* sodium iodide.

TABLE III

Cc. 0.1 *N* NaI[1]	Millivolts	Cc. 0.1 *N* NaI	Millivolts
5.0	485	16.6	380
10.0	450	16.8[2]	345
15.0	415	17.0	305
15.5	410	17.2	300
16.0	405	17.4	290
16.2	395	18.0	285
16.4	390	19.0	280

Found: Electrometric method	2.345 g. As_2O_5 per 500 cc.
Official method	2.351 g. As_2O_5 per 500 cc.
Theoretical	2.323 g. As_2O_5 per 500 cc.

[1] Factor 0.9669.

[2] End-point.

The graphic method of determining the end-point for this titration is, however, as unnecessary as in the case of trivalent arsenic. The voltage read, using a solution wherein the arsenic is just reduced, approximated very closely to 350 millivolts, under the conditions of our work. Hence by setting the sliding contact so that the millivoltmeter gave this reading and titrating till the galvanometer gave no movement or just reversed its direction, the end-point was obtained with accuracy and convenience. As in the preceding instance, it was found well to get this end-point approximately with about 0.5 cc. less sample than the final volume desired. This amount may then be added and used for the accurate estimation of the end-point by the addition of small increments of the titrating medium.

In Table IV are given some results obtained in this way and the corresponding figures obtained by the official method in which the pentavalent arsenic was determined by reduction to the trivalent form by means of hydriodic acid and titrated with iodine.

TABLE IV

MATERIAL	Per cent As_2O_5 Electrometric	Per cent As_2O_5 Official
Lead arsenate:		
Sample No. 1	32.86	32.85
Sample No. 372	26.69	26.54
Sample No. 382	32.22	31.87
Calcium arsenate	56.49	56.79
London purple A	27.77	27.56
London purple B	22.69	22.83
	G. As_2O_5 per 100 Cc.	
Sodium arsenate	0.0931	0.0929
Arsenic acid[1]	100.14	99.86

[1] Prepared from pure As_2O_3 and results calculated to per cent purity of this material.

In making the titration for As^V, care must be taken not to add the iodide solution too rapidly as the voltmeter reading changes somewhat after the addition of the solution. If, for instance, the titration is made by allowing large increments to flow in as rapidly as the buret will deliver the solution, and the reading taken at once, it will be found that this reading is too low. If such a solution is allowed to stand it will be observed that the voltmeter reading rises rather rapidly at first and then slowly for some time. If, on the other hand, the titrating solution is allowed to run in quite slowly the voltages before reaching the end-point remain constant, or at most rise only a few millivolts even when allowed to stand several hours. After passing the end-point, however, they may rise considerably. Table V shows the results of a titration made by allowing the indicated quantities of solution to flow in slowly, taking one reading at once (Column 1) and another after the voltage had become constant (Column 2), and Fig. 4 gives the data in graphical form. This change is sufficiently slow, however, to permit the operation to be carried out as outlined in a preceding paragraph with sufficient accuracy for all ordinary purposes.

TABLE V

Cc. NaI	(1) Millivolts	(2) Millivolts
0.0	360[1]	510
1.0	505	500
2.0	480	480
3.0	465	460
3.4	455	450
3.6	445	440
3.8	410	400
4.0	320	370+
4.2	290	360+
4.4	290	360+
5.0	280	355

[1] Solution stood in contact with electrode over night.

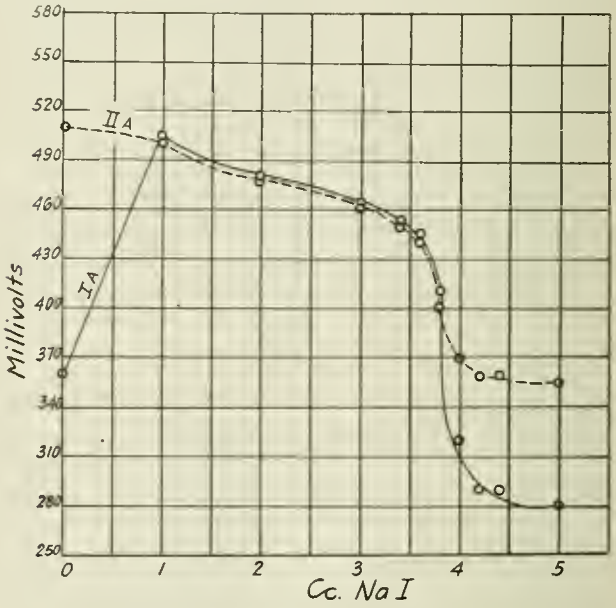

FIG. 4

SUMMARY

An electrometric method of titration had been shown to be applicable:

(1) To the determination of trivalent arsenic even in colored solutions.

(2) To the direct titration of pentavalent arsenic, with the consequent elimination of such intermediate steps as the removal of organic matter when such is present and the reduction of As^V to As^{III}.

RAPID EXAMINATION OF SHELLAC, SHELLAC VARNISH, AND LACQUER

By T. Linsey Crossley
43 Scott St., Toronto, Canada

Received March 15, 1920

The writer was called upon in the spring and summer of 1918 to examine varnish, specified to have the composition of 75 parts of shellac and 25 parts of rosin, for use in shells, to be cut with denatured alcohol, only. The specification stated that the dried gum should have an iodine number not higher than 71, according to Dr. Langmuir's modification of Wijs' method.[1]

For lack of reagents, and pressure of time in most cases, it would have been impracticable to make the above test and, therefore, some other means for approximate confirmation of adherence to specifications had to be devised.

The question of solubility of shellac in various solvents was looked into. Sulfuric ether seemed the most promising, though we found no reference to it in the literature at hand. The method referred to by Dr. Langmuir[2] calling for the use of petroleum ether has the disadvantage that pure shellac is soluble only to a slight extent in petroleum ether, and the soluble portion is not resinous but waxy.

P. C. McIlhiney[3] advocates a combined alcohol and petroleum ether determination. This method did not suit our convenience at the time (1918, July–August) because we could then obtain petroleum ether only by redistillation from gasoline in small amounts, and absolute alcohol with difficulty. We believe the sulfuric ether method, while perhaps not so exact, gave us the necessary information in less time. Among samples of rosin, grades about G to H, which we examined for shrapnel use and which we dissolved in petroleum ether, we found one that contained 20 per cent of matter insoluble in that medium, which was readily soluble in sulfuric ether. If such a rosin were used in varnish, the insoluble matter would be considered shellac by the petroleum ether method.

Upon treating a shellac rosin varnish with sulfuric ether, a flocculent precipitate comes down in a very short time, leaving an almost clear supernatant liquid which is decanted away with ease. The precipitate may be washed by repeated additions of ether and decantation.

It appeared that if the solubility of pure shellac in sulfuric ether were constant or nearly so, this property could be applied for an approximate determination of the proportions of rosin and shellac in such varnishes.

Samples of shellac of different grades, which they had every reason to believe were genuine shellac gum, were obtained by the courtesy of three varnish manufacturers. One of these was said to be of the highest quality obtainable. These gums were treated with sulfuric ether, and the following results were obtained, the ether solution being also evaporated and weighed:

	Soluble in Ether Per cent	Insoluble in Ether Per cent
1	30.0	70.0
2	28.7	70.2
3	31.8	70.1
AVERAGE	30.1	70.1

No. 3, it will be noted, totals over 100 per cent. A repetition of this determination gave 31.9 per cent soluble in ether. The presumption is that oxidation takes place. The soluble matter was found after drying to be not entirely soluble in ether.

The writer is indebted to Messrs. Rogers and Pyatt, of New York, for a sample of raw stick-lac which was examined after grinding to pass 30-mesh sieve, with the following results:

	Per cent
Woody matter, fiber, etc.	8.5
Gums not soluble in ether	70.7
Gums soluble in ether	25.0
	104.2

A second sampling of the gum gave a total insoluble in ether of 77.2 per cent, including the woody matter, as compared with 79.2 per cent above. In view of these results it was felt justifiable to assume 70 per cent as a constant for gums insoluble in sulfuric ether for technical purposes. Throughout the work commercial sulfuric ether was used, as the object was to evolve a quick test to be made in the ordinary technical laboratory.

Four samples of shellac rosin varnish were prepared by manufacturers to meet the specifications and submitted for certification of compliance. The results obtained, presuming pure shellac to be 70 per cent insoluble in ether, were:

	Rosin Per cent	Shellac Per cent
1	27	66
2	60	40
3	30	70
4	23	77

The maker of No. 2 stated that the right proportions had been used and that the shellac gum previously examined was one of the constituents. This appeared to destroy our hopes. It was tried again with similar results. Careful inquiry in the factory elicited the fact that by mistake only half the required amount of shellac had been used, confirming our results. In the case of No. 1 some of the insoluble matter was lost by accident, but the weighing of the soluble matter indicated a reasonable compliance with specifications. In view of factory conditions these results confirmed our view that a technical method for the analysis of shellac rosin varnish could be based on the solubility of lac gum in sulfuric ether, and that examination in this way would detect any marked or deliberate deviation from the specifications.

METHOD

1—Weigh in a small beaker 5 to 7 g. of varnish (have beaker weighed), place 5 g. more on other pan, pour varnish quickly until pan falls, weigh without adjusting.

2—Allow varnish to stand in warm place or, if pressed for time, place on water bath until varnish is pasty but not dry.

3—Add to beaker 50 to 60 cc. sulfuric ether (a large excess is needed as there is some alcohol in the ether and this, with what is present in the varnish, holds some of the shellac in a colloidal condition). Stir the mixture well; the insoluble matter usually clots readily and can be decanted with ease.

4—Weigh another beaker for the soluble portion which is now decanted into it through a fairly open filter paper, wash the clotted insoluble matter in the beaker with successive lots of 20 cc. ether until the washings are colorless or only faintly colored. Before pouring in the first washing it is advisable to wet the filter with a little ether from a wash bottle. The upper edges of the paper will need washing finally, as well as the funnel above the paper.

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[1] *J. Am. Chem. Soc.*, **29** (1907), 1221.

[2] *J. Soc. Chem. Ind.*, **24** (1905), 12.

[3] *J. Am. Chem. Soc.*, **30** (1908), 867.

5—Allow the washed insoluble matter to dry spontaneously in the beaker. It will be well divided and granular and almost entirely rid of ether. It can then be finished over the water bath and weighed. The small amount of insoluble matter on the filter may usually be ignored.

6—The soluble portion is evaporated rapidly in, not on, a hot water bath without flame. This keeps the upper portion of beaker hot and prevents creeping. If the soluble portion is quite clear after passage through the filter and does not cloud up on standing, it can be finished on the water bath, and not further treated. If not, proceed as in Paragraph 7.

7—The soluble portion, after drying, is washed into another beaker. Usually it is not necessary to pass through a filter as the insoluble matter is precipitated as a thin film on the lower sides of the beaker while evaporating. This film adheres to the glass and the rosin can be washed off. If the filtrate is very muddy, it would be well to take it down at once on the water bath to a pasty condition and treat it with about 50 cc. ether, filtering into a third beaker.

8—The second beaker containing the additional insoluble matter is then dried and weighed.

9—The third beaker containing the soluble portion is dried and weighed.

10—Evaporate 5 to 10 g. of the original varnish in a weighed dish with rod to determine the proportion of gums and vehicle.

In testing a sample of shellac gum it is ground to at least 30 mesh before treatment with ether, and will not need as much ether in the first place as the prepared varnish. Weigh one gram of the ground gum and moisten it in a small beaker with 5 cc. of alcohol (wood spirit will do); this softens it and permits of the ether coming into contact with all of the gum.

These results were found on one sample of varnish:

Varnish taken, 5.2 g.
Composition of varnish: Gum, 35 per cent
Spirit, 65 per cent
Gum taken = 35 per cent of 5.2 g. = 1.82 g.
Gum should contain: Rosin, 25 per cent = 0.455 g.
Shellac, 75 per cent = 1.365 g.
1.820 g.

Found insoluble in ether, 0.8825 g. = $\left(\frac{0.8825}{70} \times 100\right)$
= 1.265 g. shellac

(The insoluble matter was inclined to be slimy and there was a small loss on the filter paper.)

Rosin required = 25 per cent of gum = 0.455 g.
Ether soluble of shellac = 30 per cent of 1.365 = 0.410 g.

Required soluble in ether 0.865 g.
Found soluble in ether 0.860 g.
Shellac found = 1.265 g. = 69.5 per cent of 1.82 g.
Rosin found = 0.860 — (30 per cent of 1.265) = 0.480 g. = 26.4 per cent of 1.82 g.

We reported: Shellac 70 per cent, rosin 27 per cent, considering this a reasonable adherence to specification.

A small amount of oil had been added to this varnish, and this we believe caused the trouble in separation. Where only shellac and rosin, in proportion not over 30 per cent rosin, are cut in denatured alcohol, we have been able to get results close enough for the purpose in 2 or 3 hrs.

APPARATUS

Three beakers, 125 cc. capacity; one 2.5 in. funnel, filter stand, stirring rods, wedgewood mortar and pestle, 30-mesh sieve, balance sensitive to 1 mg., commercial sulfuric ether, and denatured alcohol. These can be found in any paint laboratory.

DISCUSSION

The results are positive, the actual substances being weighed, soluble and insoluble. Their properties and appearance are sufficient demonstration of their difference in character. The results obtained by iodine absorption are indirect and deductive, the iodine absorption of rosin being given by different writers as from 176 per cent to 235 per cent and that of shellac from 9 per cent to 31 per cent. We believe, therefore, that the iodine absorption method has no advantage over that of separation outlined above, and if oil were to be added to the varnish its absorption would introduce a third unknown quantity.

In our work we have obtained fairly good results where linseed oil has been used, but in such cases care must be taken to avoid oxidation of the oil by heating the varnish when the alcohol is being eliminated. In these cases very little evaporation to clot the insoluble matter should be attempted.

Varnishes containing very much rosin and very little shellac give difficulty owing to the finely divided ether precipitate, but on standing over night the soluble matter may generally be decanted. If not, it was always found practicable to filter and weigh the soluble portion.

We did not find the use of tared filters advisable as the insoluble matter at times sticks to the sides of the beaker.

Both the insoluble matter and the rosin should be subjected to temperatures up to 110° C. or 120° C. to eliminate the last traces of alcohol and water, the latter introduced to some extent by condensation from the air.

We have also found the method useful for determining the percentage of shellac in shellac-turmeric lacquers. We found that of the 20 per cent or so of the turmeric that was suspended in the spirit practically all was soluble in sulfuric ether.

Incidental to the above work, the solubility of shellac in petroleum ether and commercial wood alcohol was determined. The results may be of interest:

The extraction with petroleum ether was made by soaking the gum, ground to 30 mesh, at room temperature for 24 hrs. at a time for 5 days. The petroleum ether had a boiling point of 85° C.

SOLUBILITY IN PETROLEUM ETHER

	Commercial Shellac Per cent	Stick-lac Per cent
1st and 2nd extractions (48 hrs.)	0.40	3.01
3rd extraction (24 hrs.)	0.45	0.61
4th extraction (24 hrs.)	0.25	0.31
5th extraction (24 hrs.)	nil	nil
	1.10	3.93

Two other samples of commercial shellac gave solubilities of 1.83 per cent and 1.4 per cent in petroleum ether. In view of these results care should be taken to ensure complete extraction before reporting solubilities.

SOLUBILITY IN WOOD ALCOHOL

Commercial shellac	91.66 per cent
Stick-lac	81.4 per cent

The stick-lac was that referred to, containing 8.5 per cent of woody matter.

I wish to acknowledge indebtedness to my colleague, Mr. J. D. Stuart, who did much of the work incidental to the above investigation.

THE FREEZING POINTS OF MIXTURES OF SULFURIC AND NITRIC ACIDS[1]

By Walter C. Holmes

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Mixtures of sulfuric and nitric acids, commonly designated as mixed acids, are used in enormous amounts in the chemical industry in nitration processes, as carried out in the explosive and dye industries. Owing to a case where a mixed acid had become frozen during storage, under conditions where freezing seemed improbable, determinations of the freezing points of a large number of mixed acids were carried out in this laboratory. The original object of the work was simply to obtain empirical data regarding the temperatures of freezing for different mixtures. The results, however, were of exceptional interest, as indicating the formation of a definite chemical compound between sulfuric and nitric acids. While the thorough explanation of the phenomena observed was beyond the scope of the work, it is believed that the presentation of these results will be of value as an addition to the knowledge of mixed acids.

The only chemical compound of sulfuric and nitric acids which could be found in the literature is that mentioned by Weber,[2] who gives it the composition $4SO_3.N_2O_5.3H_2O$, though this composition does not seem proved. The most thorough study of the properties of mixed acids appears to have been carried out by Saposchnikow,[3] who investigated particularly the vapor pressures, specific gravities, and conductivities of such mixtures in all proportions.

EXPERIMENTAL

Three sets of mixed acids were made up of 100, 95, and 103 per cent total acidities, respectively, so that in each set of acids the only variables were the sulfuric acid and the nitric acid contents. The nitric content of the mixtures was varied from zero to approximately 50 per cent in the 100 and 95 per cent mixtures, and up to about 30 per cent in the 103 per cent mixtures. In all cases the compositions of the mixtures were determined by careful analysis.

The freezing was carried out in test tubes of about one inch diameter, the thermometer being used as stirrer. The test tubes were immersed in an insulated bath. The freezing mixture consisted of ether and carbon dioxide snow, by means of which temperatures as low as —72° C. were obtained. Where possible, a standardized mercury thermometer was used, but at extremely low temperatures a toluene-filled thermometer which had previously been compared with the mercury thermometer, was used. Extreme supercooling was met with, one case occurring where the acid did not freeze at a temperature over 60° C. below the true freezing point, as subsequently determined. As a rule, however, solidification could be induced by inoculation of the sample with a small crystal of frozen acid, care being taken that this crystal should be from an acid of similar composition. Precautions were also taken that, in the final determinations on an acid, the surrounding bath should not be more than a few degrees lower than the freezing point of the acid.

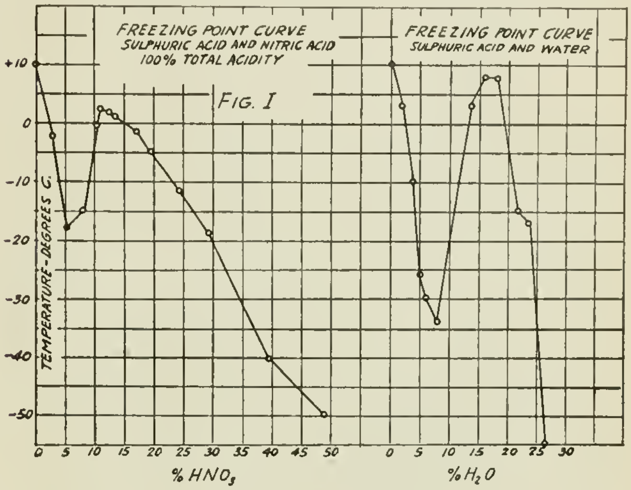
FIG. I

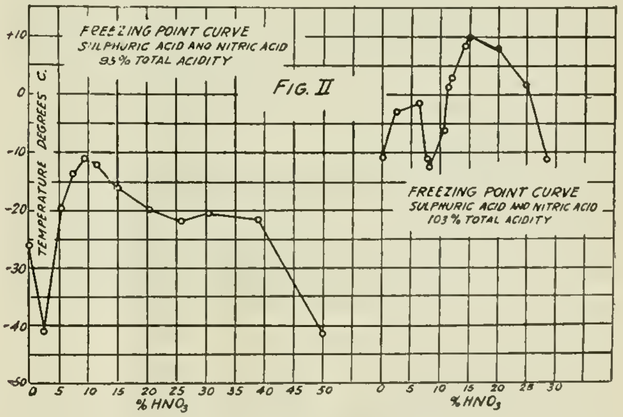
FIG. II

The exact procedure was as follows: A sample was frozen by cooling below the true freezing point and by subsequent inoculation or vigorous stirring, as the case demanded. The temperature of freezing was noted, this temperature being taken at the highest point reached, as in all cases a rise in temperature took place at the time of solidification. The bath was then regulated to not more than 4° or 5° below the temperature recorded, and a second sample was frozen. This procedure was repeated until the highest point at which an acid would freeze had been found and checked several times.

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[1] Read at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

[2] *Ann. Phys. Chem.* (Pogg.), **142** (1871), 602.

[3] *Z. physik. Chem.*, **49**, 697; **51**, 609; **53**, 225 (1904-1905).

The freezing point values given in the table were obtained by this method:

FREEZING POINTS OF MIXED ACIDS

Acid No.	Composition (Per cent) Actual H_2SO_4	Actual HNO_3	$HNOSO_4$	H_2O	Freezing Point ° C.
	Series A—100% Total Acidity				
1	100	...	..	..	+10.0
2	96.24	3.05	0.24	0.47	—2.2
3	93.73	5.38	0.30	0.59	—18.2
4	91.95	7.83	0.39	—0.17	—15.1
5	89.33	10.20	0.49	—0.02	—0.7
6	88.67	10.80	0.53	0.00	+2.3
7	86.93	12.61	0.54	—0.08	+2.0
8	84.93	13.76	0.63	0.68	+1.0
9	84.85	13.90	0.64	0.61	+1.4
10	81.50	16.93	0.73	0.84	—1.4
11	82.77	17.06	0.36	—0.19	—1.5
12	81.68	17.20	0.76	0.36	—1.6
13	78.78	19.70	0.85	0.67	—5.1
14	74.06	24.59	1.04	0.31	—11.5
15	68.87	29.24	1.65	0.24	—19.0
16	58.83	39.40	1.60	0.17	—40.0 (approx.)
17	48.95	48.84	1.93	0.28	—50.0 (approx.)
	Series B—95% Total Acidity				
1	94.96	...	..	..	—26.0
2	92.52	2.35	0.05	5.08	—41.0
3	89.11	5.69	0.04	5.16	—19.5
4	87.72	7.36	0.03	4.89	—13.5
5	84.50	9.75	0.19	5.56	—11.0
6	82.81	11.72	0.02	5.45	—12.0
7	78.64	15.20	0.40	5.76	—16.0
8	75.22	20.40	0.04	4.34	—20.0
9	70.05	25.70	0.07	4.18	—22.0
10	64.82	30.15	0.15	4.87	—20.5
11	54.18	39.02	1.13	5.67	—21.8
12	44.04	49.09	1.33	5.54	—41.3
	Series C—103% Total Acidity				
1	103.0	...	..	..	—9.3[1]
2	100.25	2.48	0.64	—3.37	—2.8
3	96.87	6.31	0.12	—3.30	—1.5
4	94.93	7.89	0.65	—3.47	—11.0
5	94.44	8.15	0.42	—3.01	—12.3
6	92.07	10.78	0.23	—3.08	—6.0
7	90.36	11.74	0.58	—2.68	+1.7
8	90.38	12.02	0.58	—2.98	+3.0
9	88.64	14.25	0.77	—3.66	+8.5
10	87.30	15.52	0.33	—3.15	+10.5
11	82.71	20.08	0.39	—3.18	+8.0
12	77.48	25.02	0.59	—3.09	+2.0
13	72.85	28.63	0.79	—2.27	—11.0

[1] The freezing point given, —9.3°, is interpolated from the table of Knietsch, *Ber.*, **34** (1901), 4100. At the time this work was being carried out, no fuming sulfuric acid, free from small amounts of nitric acid was available.

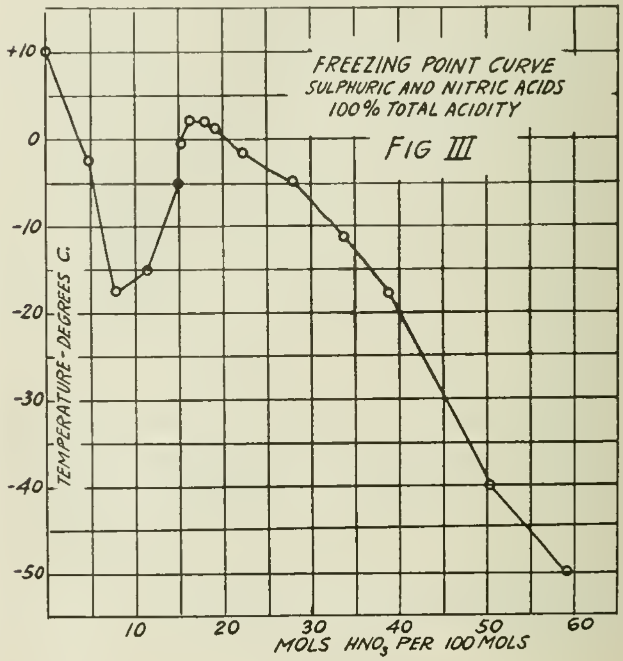
DISCUSSION OF RESULTS

The results tabulated above show that the addition of nitric acid first depresses the freezing point of sulfuric acid. On addition of further amounts of nitric acid, a rapid rise in the freezing point takes place, until a maximum is reached. A general similarity is seen between the freezing-point curves for the three sets of acids. The curves for the mixtures containing 95 per cent and 103 per cent total acidities (Fig. II), however, are somewhat complicated by the presence of a third component, water in the one case and free sulfur trioxide in the other. Two maxima occur in each curve. For this reason, no attempt has been made to explain the form of these curves.

A marked similarity, moreover, is seen to exist between the freezing-point curve of sulfuric acid and nitric acid (100 per cent total acidity) and that of sulfuric acid and water (Fig. I).[1] In the latter case, the curve falls to a minimum of —34° C. when 8.4 per cent water is present; then rises to a maximum of +8.0° C. with a water content of 15.5 per cent. In the case of sulfuric acid and nitric acid, the minimum comes at —18.2° C., with a nitric content of 5.5 per cent, and the maximum at +2.3°, when approximately 11.0 per cent of nitric acid is present.

The maximum in the sulfuric acid-water curve represents a definitely known compound between sulfuric acid and water, the dihydrate $H_2SO_4.H_2O$. Reasoning from analogy, it seems probable that the maximum in the sulfuric acid-nitric acid curve also represents a definite compound, between sulfuric and nitric acids, since the addition of either component will depress the freezing point of the mixture. Further evidence in favor of the formation of a definite compound is the fact that it was repeatedly found that inoculation of the acid mixtures with a crystal of sulfuric acid would not induce solidification. The use of a crystal of frozen mixed acid was necessary in almost all cases.

The maximum point in the sulfuric acid-nitric acid curve comes at a point where the nitric acid content is 10.80 per cent. It is significant that Saposchnikow found the density of such mixtures to attain a maximum when the nitric content was between 10 and 12.5 per cent. The acid mixture having a nitric content of 10.8 per cent represents almost exactly the combination $5H_2SO_4.HNO_3$.



In the freezing-point curve for sulfuric acid and water, while the maximum comes at the composition $H_2SO_4.H_2O$, the preceding minimum comes at the composition H_2SO_4-$^1/_2H_2O$. It may be a coincidence, but it is at least an interesting one that in the sulfuric-nitric acid curve the maximum comes at the composition $5H_2SO_4.HNO_3$ and the preceding minimum at the approximate composition $5H_2SO_4$-$^1/_2HNO_3$.

Saposchnikow did not reach any conclusion as to whether a compound was formed between sulfuric and nitric acids. It was his belief, however, that in mixed acids with a sulfuric content higher than 80 per cent, the nitric acid was dehydrated, with formation of nitric anhydride. This view of Saposchnikow, regarding the condition in which nitric acid is present in mixed acids, is questioned by Marshall.[1]

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[1] The freezing-point curve for sulfuric acid and water is based on data given by Knietsch, *Ber.*, **34** (1901), 4100.

[1] "Explosives," 2nd Ed., **1917**, p. 123.

SUMMARY

1—Freezing-point determinations were made on three sets of mixtures of sulfuric and nitric acids, having total acidities of 100, 95, and 103 per cent, respectively, and nitric contents varying from zero to 50 per cent.

2—The freezing-point curve for the 100 per cent acidity mixtures was found to reach a minimum when the nitric acid content was 5.4 per cent. The maximum was attained with a nitric acid content of 10.8 per cent. The curve showed a marked resemblance to that of sulfuric acid and water.

3—It seemed probable that the composition, at the above maximum, represented a definite chemical compound between sulfuric and nitric acids, the acids at that point being present in the proportion $5H_2SO_4$-HNO_3.

4—The freezing-point curves for the 95 and 103 per cent mixtures were complicated by the presence of a third constituent. No attempt, therefore, was made to explain them.

HYGROSCOPICITY OF BY-PRODUCT COKE[1]

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The experiments described in this paper were undertaken in order to obtain data as to the amount of moisture absorbed by dry pulverized coke on exposure to air of varying humidity in connection with methods[2] used in many commercial laboratories for the analysis of coke.

In these methods the sample for total moisture determination is taken from the regular sample for analysis by reserving one or more rejected quarters after the sample has been crushed to half-inch size. Moisture is determined in 10 lbs. or more by drying to approximately constant weight at a temperature of 105° C. The laboratory sample for analysis is prepared by crushing and reducing the regular sample until about one pound of 40-mesh material remains. A sufficient amount of this 40-mesh material is transferred to a bottle and dried for one hour at 105° C. No moisture determination is made in the laboratory on the dried material, it being assumed that the coke will not absorb appreciable amounts of moisture from the air. It is evident that, if the pulverized sample of coke did absorb appreciable amounts of moisture between the time of drying and the weighing of the various portions for analysis, the analysis would be in error corresponding to the amount of moisture absorbed. The volatile matter determination, especially, would be too high.

STANDARD MOISTURE DETERMINATION METHODS

When a high degree of accuracy is desired, the moisture in coke is determined in two stages. The coke is crushed to one-half or one-quarter inch size and air-dried to approximately constant weight at a temperature of 30° to 35° C. The air-dry sample is then pulverized to 60 mesh and the residual moisture determined by heating a one-gram sample for one hour at 105° C.[1] Experiments made by the Bureau[2] have shown that total moisture in coke can be determined with adequate accuracy (±0.5 per cent) for most purposes by simply heating to constant weight a large sample of lump coke, in any convenient oven, or on a stove, hot plate, or steam coil, at a temperature of 105° to 200° C.

The standard methods of analyzing coke as given by the American Society for Testing Materials[3] state that the total moisture shall be determined by drying the entire sample received at the laboratory without any preliminary crushing to constant weight at a temperature of not less than 104° or more than 200° C., and that the loss in weight is to be calculated as percentage of moisture which shall constitute the total moisture in the coke as received in the laboratory. The sample for analysis crushed to a fineness of 60 mesh is prepared from the dried coke without any regard to changes in moisture content. Moisture is then determined on the 60-mesh material by heating a one-gram sample of the coke for one hour in a suitable oven at a temperature of 104° to 110° C. The moisture obtained on the 60-mesh material is used simply to calculate the determinations made on this material to a dry basis. The total moisture as determined on the lump size sample is taken as the total moisture content of the coke, and the air-dry figures, are then calculated to the "as received" condition.

OUTLINE OF EXPERIMENTS

Four samples of coke were selected for the tests, one sample of beehive coke and three samples of by-product coke. These samples had been previously air-dried and crushed to pass through a 60-mesh sieve. The analysis and origin of these samples are given in Table I.

Table I—Air-Dried 60-Mesh Coke Samples Used in Tests

No.	Origin of Sample	Per cent Moisture	 Volatile Matter	 Fixed Carbon	 Ash	 Sulfur
31177	Connellsville 72-hour beehive foundry coke	0.15	1.56	89.09	9.20	0.78
31075	By-product furnace coke from Franklin County, Ill., coal	0.98	2.53	83.79	12.70	0.88
33754	By-product domestic size coke (source of coal unknown).	0.50	1.98	85.79	11.73	0.82
31677	By-product domestic size coke from Pittsburgh bed coal	0.56	2.80	79.46	17.18	0.89

One-gram samples of the 60-mesh coke were weighed in duplicate into porcelain capsules, dried in an oven for one hour at 105° C., cooled over sulfuric acid in desiccators, and weighed, the loss in weight being recorded as moisture. In order to prevent any changes in moisture during the weighing of the samples, all weighings throughout the test were made by placing the porcelain capsules containing the samples in glass weighing dishes provided with tightly fitting ground caps.

The uncovered crucibles and contents were placed in one-quart Mason jars containing mixtures of sul-

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[1] Published by permission of the Director of the Bureau of Mines.

[2] United States Steel Corporation, "Methods for the Commercial Sampling and Analysis of Coal, Coke, and By-products," 1916, p. 18.

[1] F. M. Stanton and A. C. Fieldner, Bureau of Mines, *Technical Paper* 8 (1913), 7.

[2] A. C. Fieldner and W. A. Selvig, *Ibid.*, 148 (1617), 14.

[3] *Am. Soc. Test. Mat. Standards*, 1919, 711.

Table II—Per cent Moisture Absorbed by 1-G. Coke Samples after Drying at 105° C. for 1 Hr., when Exposed to Air of 25, 50, and 80 Per cent Humidity at 28° C.

No.	Source of Coke	Per cent Moisture on 1-G. Sample Heated 1 Hr. at 105° C.	Hours of Exposure	Per cent Moisture Absorbed								
				25 Per cent Humidity			50 Per cent Humidity			80 Per cent Humidity		
				1	2	Av.	1	2	Av.	1	2	Av.
31177	Connellsville 72-hr. beehive foundry coke	0.15	1	0.15	0.15	0.15	0.21	0.21	0.21	0.53	0.52	0.52
			6	0.19	0.17	0.18	0.42	0.43	0.42	0.68	0.67	0.68
			18	0.16	0.15	0.16	0.44	0.45	0.44	0.70	0.67	0.68
31075	By-product furnace coke from Franklin Co., Ill., coal...	0.98	1	0.39	0.43	0.41	1.12	1.05	1.08	1.54	1.63	1.58
			6	0.53	0.54	0.54	1.77	1.73	1.75	2.25	2.32	2.28
			18	0.52	0.56	0.54	1.77	1.75	1.76	2.28	2.35	2.32
33754	By-product domestic size coke (source of coal unknown)	0.50	1	0.26	0.26	0.26	0.75	0.75	0.75	1.49	1.43	1.46
			6	0.41	0.41	0.41	0.98	1.08	1.03	1.76	1.78	1.77
			18	0.40	0.41	0.40	1.22	1.14	1.18	1.82	1.79	1.80
31677	By-product domestic size coke from Pittsburgh bed coal	0.56	1	0.19	0.19	0.19	1.00	1.02	1.01	1.30	1.18	1.24
			6	0.52	0.55	0.54	1.15	1.11	1.13	1.54	1.52	1.53
			18	0.50	0.52	0.51	1.28	1.35	1.32	1.56	1.54	1.55

furic acid and water to give a range of humidity in the air above the acid of 25, 50, and 80 per cent at 28° C. The acid was placed in the jars to a depth of about 2 in. and the porcelain capsules were supported by glass triangles in the air above the acid.

The jars containing the acid were completely submerged in a water bath provided with a thermostat which maintained a temperature of 28° C. (±0.2° C.) throughout the test. After the jars and contents had been submerged in the water for a sufficient time to come to the temperature of the bath, the porcelain capsules containing the dried coke samples were heated in an air oven to approximately 40° C., and quickly placed in the jars above the acid. This preliminary heating to 40° C. was made to prevent any condensation of moisture on the capsules or contents which might result if the capsules and contents were at a lower temperature than the air in the jars.

The various coke samples placed in the jars giving humidities of 25, 50, and 80 per cent at 28° C. were allowed to remain for periods of 1, 6, and 24 hrs. at each of these humidities. At the end of these periods the capsules containing the samples were quickly removed, placed in covered weighing dishes, allowed to come to room temperature, and weighed. The results of these tests are given in Table II.

Tests were also made on one-gram samples of the same cokes weighed in porcelain capsules, dried for one hour at 105° C., and allowed to stand exposed to the air in the laboratory, weighings being made at intervals covering periods of 24 hrs. Temperature and humidity readings were made at the time of the different weighings. The results of these tests are given in Table III.

Table III—Per cent Moisture Absorbed by 1-G. Coke Samples after Drying at 105° C. for 1 Hr., when Exposed to Air of Laboratory

No.	Per cent Moisture on 1-G. Undried Coke (Heated 1 Hr. at 105° C.)	Average Temp. ° C.	Average Relative Humidity Per cent	Per cent Moisture Absorbed by Dry Coke							
				Hours of Exposure							
				1	1.5	2	3	4	5	7	24
31177	0.15	22	20	0.06	0.08	0.09	0.10	0.10	0.11	0.14	0.11
31075	0.98	24	27	0.33	0.41	0.47	0.49	0.49	0.54	0.54	0.50
33754	0.50	23	25	0.18	0.22	0.22	0.23	0.25	0.25	0.29	0.37
31677	0.56	23	26	0.17	0.18	0.22	0.26	0.26	0.30	0.35	0.46

DISCUSSION OF RESULTS

The range of humidity from 25 to 80 per cent, as shown in Table II, covers conditions that may occur in the average laboratory during the year. During the winter months when the temperature of the laboratory air is considerably higher than that of the outdoor air, a relatively low humidity is likely to prevail. Such conditions prevailed at the time of making the tests, the laboratory air having a humidity of about 25 per cent. During the summer months when the temperature of the laboratory air and the out-door air is about the same, a relatively high humidity may prevail, and conditions comparable to the 50 and 80 per cent humidity of Table II would result.

As shown in Tables II and III, the hygroscopicity of each coke was different. The three samples of by-product coke absorbed moisture much more readily than the sample of beehive coke. The cokes varied as to the rapidity with which they absorbed moisture and as to the amounts absorbed when they reached equilibrium with respect to the moisture in the surrounding air. At 50 per cent humidity two of the by-product cokes absorbed 1 per cent moisture in one hour. The gain in moisture between the 6- and 18-hr. intervals was small, showing that under the conditions of the test the cokes had practically come to an equilibrium with the moisture in the air in less than 6 hrs. Under these conditions the beehive coke had absorbed 0.4 per cent moisture, and one of the by-product cokes had absorbed 1.7 per cent moisture.

CONCLUSIONS

The tests show that dry pulverized by-product coke rapidly absorbs moisture in appreciable amounts and that different cokes vary considerably in hygroscopicity. The by-product cokes tested were more hygroscopic than the beehive coke. This absorption may, under humidity conditions such as exist in the average laboratory, be sufficient to cause appreciable errors in the analysis unless it is determined and accounted for. The greatest error would occur in the volatile matter determination, as any absorbed moisture would be directly included in this determination. A safe procedure is to make a moisture determination on the laboratory sample and take this result into consideration in calculating the analysis to the dry coke basis.

ACKNOWLEDGMENT

Acknowledgment is made to Mr. A. C. Fieldner, supervising chemist of the Pittsburgh Station of the Bureau of Mines, for helpful suggestions as to the method of making the hygroscopicity tests.

THE DETERMINATION OF SULFATE IN SULFONATED OILS[1]

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During a recent visit to the author's laboratory Prof. A. W. Thomas showed that sulfuric acid can be extracted quantitatively from leather by means of a solution of monosodium phosphate. The writer has found that with a sulfonated oil this solution causes a practically complete separation of oil from solution in a remarkably short time and that the solution contains all of the free and none of the combined sulfates of the original oil. It was at once apparent that this phosphate solution possessed real advantages over the saturated sodium chloride solution and ether used in the ordinary method of determining uncombined sulfates in sulfonated oils.

FREE SULFATE

The usual procedure for free sulfate is to dissolve 4 or 5 g. of the oil in ether, shake out several times with saturated salt solution, combine these washings, dilute, filter, and precipitate the sulfate with barium chloride. The use of ether is necessary in this method because the salt solution when used alone does not readily cause a clear separation of oil and solution; in fact, it not only fails to give a sharp separation, but it extracts only a small portion of the free sulfate, giving in one case only 0.06 per cent when 0.20 per cent was actually present.

On the other hand, the phosphate solution, without the addition of an organic solvent, extracts all the free sulfate and produces a sharp separation in less time than when sodium chloride and ether are used. A 25 per cent phosphate solution gives a sharp separation in about 5 min., but for general work a 10 per cent solution is quite satisfactory. When the ordinary method is used with oils containing much water, the salt solution becomes so dilute that it fails to give a clear separation, in which case it has been found necessary to add dry salt and shake vigorously until the solution became nearly saturated. No difficulty from this source has been found with the 10 per cent phosphate solution, even with oils containing as high as 35 per cent water.

In a series of tests it was proved that one extraction with a 10 per cent phosphate solution is quite as effective in removing the free sulfates from an oil as the customary three with brine and ether. Comparative results for four typical oils are given in Table I.

Table I—Per cent of Free Sulfate (SO_3) in Four Typical Oils

	(1)	(2)	(3)	(4)
Brine and ether (3 extractions)	0.10	0.20	0.33	0.18
Phosphate solution (1 extraction)	0.12	0.21	0.33	0.20

In order to test the completeness of the extraction, definite amounts of anhydrous sodium sulfate were added to portions of an oil containing only 0.04 per cent of free sulfate and these samples were then extracted four times with 10 per cent phosphate solution. The results in Table II show that the bulk of the sulfate is removed in the first extraction and the remainder in the second extraction.

Table II—Per cent SO_3 Extracted by Phosphate Solution

Per cent Free SO_3 Actually Present	1st Extraction	2nd Extraction	3rd Extraction	4th Extraction
0.27	0.21	0.03	Trace	None
0.57	0.53	0.06	Trace	None
0.98	0.93	0.06	Trace	None

Where the amount of water in the oil is known, complete separation of the solution from the oil is unnecessary. Five samples, of known sulfate content, were prepared, measured amounts of phosphate solution were added, the mixtures were shaken and allowed to separate, and aliquot portions of the solution were taken for analysis. Dilution caused by the water in the oil is allowed for in the calculation. This method of procedure is extremely rapid and the results in Table III show that it is quite accurate. If the aliquot portion is taken before the solution is quite clear, the oil must be filtered off before boiling with the barium chloride solution.

Table III

Per cent Free SO_3 Actually Present	Per cent SO_3 Found by Taking Aliquot Portion of the Phosphate Solution
0.10	0.12
0.20	0.21
0.27	0.26
0.57	0.57
0.98	0.97

TOTAL SULFATE

A common method of estimating the amount of total sulfate in sulfonated oils is to boil with hydrochloric acid solution to liberate the combined sulfate, cool, add petrol to dissolve the oil, wash in a separatory funnel several times with water, combine the washings, and precipitate the sulfate with barium chloride. The organic solvent can be dispensed with, just as in the determination of free sulfate, by using the 10 per cent phosphate solution. Two extractions with the phosphate solution proved sufficient to extract all of the sulfate. A comparison of the two methods is given in Table IV, along with determinations made by a fusion method. In boiling the oil with hydrochloric acid we have always experienced difficulties due to the bumping of the mixture. We have consequently found it preferable to use a fusion method, which consists of evaporating the oil with sodium carbonate, igniting, fusing, dissolving the residue and boiling with sodium peroxide, acidifying, and precipitating as usual with barium chloride.

Table IV—Total SO_3 by Different Methods

	Per cent Total SO_3 Found in	
	Sulfonated Castor Oil	Sulfonated Neat's-foot Oil
Extraction with water, using petrol	3.39	2.78
Extraction with phosphate solution alone	3.44	2.80
By the fusion method	3.31	2.88

RECOMMENDED METHOD

For the determination of uncombined sulfate in any ordinary oil, we recommend the following procedure: Weigh from 20 to 40 g. of oil into a separatory funnel, add 100 cc. of a 10 per cent solution of monosodium phosphate, shake, allow the oil and solution to separate, draw off the major portion of solution, and filter free from any oil particles, acidify 50 cc. of the filtrate, and precipitate the sulfate with barium chloride. In calculating the per cent of free sulfate in the original oil, make allowance for the dilution of the solution by the water of the oil.

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[1] Presented before the Section of Leather Chemistry at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

LABORATORY AND PLANT

POTASH FROM KELP. III—THE PRELIMINARY EXAMINATION OF KELP DISTILLATES[1]

By G. C. Spencer

U. S. Kelp Potash Plant, Summerland, California

Received March 9, 1920

The process whereby kelp is treated at the experimental plant for the extraction of potash and other values as operated by the U. S. Department of Agriculture at Summerland, Cal., prescribes its reduction to a charcoal from which potassium chloride and iodide are easily leached. This reduction is essentially a destructive distillation and is best carried out in closed retorts. Under such conditions large quantities of distillation products are obtained, and it was the purpose of the research here described to determine their nature, from the point of view of their possible commercial value.[2]

The work was begun in the Chemical Section of the Forest Products Laboratory, at Madison, Wis., in February 1918, that laboratory being chosen on account of its superior equipment for handling tarry distillates. In addition to tar distillations, the writer made sixteen experimental distillations of dried kelp at low temperatures in the wood distilling retort of the laboratory.[3]

This low-temperature kelp distillation showed that the nature of kelp tar varies greatly with the temperature as in the case of coal distillations. Since dried kelp contains about the same percentage of nitrogen as bituminous coal (about 2 per cent) it was hoped that the presence of this nitrogen would promote the formation of aromatic compounds in the distillate at higher temperatures corresponding to those used in destructive coal distillation. Subsequent distillations of kelp at high temperatures in Summerland, Cal., did not, however, warrant this speculation.

Kelp tar then stands in a class by itself as regards its properties and constituents. Three series of investigations were conducted to determine the nature of the condensates from high-, intermediate-, and low-temperature distillations of kelp, respectively.

EXAMINATION OF LOW-TEMPERATURE TAR

The so-called low-temperature kelp tar made in the wood retort at the Forest Products Laboratory was produced at temperatures ranging from 243° to 305° C. Each charge of kelp varied from 25 to 30 lbs. The amount of crude tar reported in connection with the various distillation runs averaged 1.1 per cent, which was, roughly speaking, double the actual amount of tar present owing to suspended water, which could be removed only by subsequent treatment. The amount of dried tar varied from 45 to 65 per cent of the crude tarry substance taken. This low recovery of tar from kelp is probably due to the slow rate of heating and the low maximum temperature (320° C.), which did not entirely expel the last of the volatile organic matter from the kelp material in any case.

DRYING ON LABORATORY SCALE—The systematic examination of kelp tar showed that the entrained water must be removed before the tar proper could be distilled, since its presence caused the latter to froth and overflow into the condenser with resultant inconvenience and delay. This difficulty was overcome by heating the tar to a temperature of 110° to 140° C. with an oil or sand bath, while a current of air was drawn through the tar and condenser into a receiving apparatus. Later on it was found necessary only for the air to pass through the flask to sweep out the water and oil vapors as they formed, and the practice of bubbling air through the liquid was discontinued. This method of drying the tar was troublesome and time-consuming and out of the question for larger quantities of material. A better method which was followed at Summerland will be described later.

The tar thus prepared was nearly free from moisture and could be distilled with a free flame. It was a black viscous liquid having a specific gravity ranging from 1.093 to 1.102, and rather more pasty in its consistency than that made in Summerland.

FRACTIONATION—When 406 g. of this tar were distilled with a free flame, 182.4 g. of an oily distillate with a characteristic odor came over between 230° and 270° C. On allowing this oil to stand in a separatory funnel for several hours it separated into two layers, the upper of which was dark in color, had a specific gravity of 1.022, and weighed 139.1 g. The light red lower layer proved to be an aqueous solution of ammonium salts and of a water-soluble organic body similar to, if not identical with, that which remains when the aqueous kelp distillate is evaporated. A fuller discussion of this water-soluble compound will be given below.

The upper layer of oil was shaken with successive portions of 30 and 10 cc. of 4 *N* sulfuric acid to remove all the bases. As is generally the case with such kelp oils, a considerable amount dissolved in the dilute acid, the total amount of bases and other compounds thus removed being 25.0 per cent. To determine whether the oils in the sulfuric acid were in a state of emulsion it was shaken with an equal volume of saturated sodium chloride solution. Only a slight amount of oil separated on standing. The sulfuric acid solution was next washed with ether, then the acid was carefully neutralized with sodium carbonate solution to liberate any weaker bases without setting ammonia free. The brown oil which separated was taken up with ether and the ether solution shaken with dilute acetic acid to form acetates of the free bases if any were present. On evaporating off the ether the residue contained no salts.

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[1] The second paper of this series entitled "Potash from Kelp. II—Experimental Distillation of Kelp at Low Temperatures," by the present writer, appeared in This Journal, **12** (1920), 682.

[2] E. C. C. Stanford, "The Distillation of Seaweed," *Chem. News*, **34**, No. 888, 237. D. M. Balch, "On the Chemistry of Certain Algae of the Pacific Coast," This Journal, **1** (1909), 777. J. W. Turrentine, "Note on the Distillation of Kelp," *Proc. 8th Intern. Cong. Appl. Chem.*, **15** (1912), 313. J. S. Burd, "The Economic Value of Pacific Coast Kelps," California Agr. Exp. Sta., *Bull.* **248** (1915), 183.

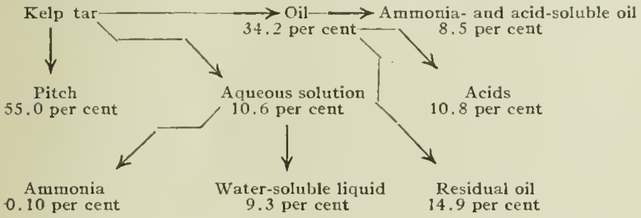
[3] *Loc. cit.*

The oil which had been shaken with sulfuric acid was next shaken with successive portions of 4 *N* sodium hydroxide solution (30 cc. and 10 cc. each) to take up acids and phenols. The crude tar acids, which were liberated from the caustic soda solution by sulfuric acid, differed distinctly from those of the higher temperature tar in odor, and possessed a specific gravity of only 0.979. After standing for some time crystals were formed, apparently voluminous, but weighing very little when separated and purified. They were recovered from the oil by filtering through a dry filter paper and washing with low-boiling gasoline. After removing as much as possible of the excess oil by pressing between sheets of filter paper, the crystals were dissolved in glacial acetic acid and the solution evaporated slowly, at first on the steam bath, later at room temperature. The crystals thus obtained melted at 63° C. This, however, is not a trustworthy value, but the small yield did not permit another recrystallization. Alcohol and ether were only partial solvents.

The main bulk of liquid acids gave no test for phenols when the oily mixture was shaken with sodium carbonate and the remaining oil treated with bromine. It is probable that none could be formed at the low distillation temperature.

The residual kelp oil made in this way is in general similar to that made from other kelp tars, although it has a different odor.

The low-temperature kelp tar has a composition which may be outlined as follows:


Kelp tar
Oil 34.2 per cent
Ammonia- and acid-soluble oil 8.5 per cent
Pitch 55.0 per cent
Aqueous solution 10.6 per cent
Acids 10.8 per cent
Ammonia 0.10 per cent
Water-soluble liquid 9.3 per cent
Residual oil 14.9 per cent

Low-temperature kelp tar has fewer desirable properties, from the industrial point of view, than that made at higher temperatures and so far as known at present its chemical constituents would be of little more than academic interest.

PITCH—The pitch from the low-temperature tar was black and brittle and had a specific gravity of 1.11; its melting point stood at 103°, and in general the sample did not seem to have unusual or valuable properties.

EXAMINATION OF TAR PRODUCED AT INTERMEDIATE TEMPERATURES

The tarry product from intermediate temperature distillation was a mixture of pasty black tar with varying amounts of water (averaging 40 per cent), and about 20 per cent volatile oil. The odor of the tar suggested the simultaneous presence of various sulfur and nitrogen compounds.

The anhydrous tar prepared from this crude material had a specific gravity of 1.092. Its nitrogen content was 3.17 per cent and it contained no free carbon.

TABLE I—SUMMARY OF RESULTS OF DISTILLATION OF DRIED TAR

	Per cent
First Runnings:	
Water	2.4
Oil	1.4
Fractions:	
200°–210°	6.0
210°–240°	16.8
240°–275°	12.0
Pitch (by difference)	61.4

The entire oily distillate consisted of phenolic compounds (tar acids), neutral compounds (residual oil), ammonium compounds, and some water-soluble liquids. The fraction that came over between 240° and 275° C. darkened very rapidly on exposure to the air. The above fractions are not natural distillation cuts. The temperature rose so uniformly while the distillate was coming over that only arbitrary temperature ranges can be assumed.

The objectionable odor of the oils during distillation was considerably lessened by receiving the distillates in approximately 4 *N* sulfuric acid. The sulfuric acid not only removed ammonia but also dissolved a constituent of the oil. When an attempt was made to recover the bases by liberating them with alkali and shaking out with ether this acid-soluble oil separated with the ether and remained with the ammonium salts. It was probably identical with the acid-soluble oil mentioned under the heading of "Low-Temperature Tar."

Attempts were first made to fractionate the distillate directly from the dry tar, but the later practice was to collect the entire oily distillate at once, and to extract this as follows: The oil from the distilling flask was received in 30 cc. sulfuric acid (approximately 4 *N*) and was shaken out once more with 10 cc. of the acid; then finally washed with a saturated common salt solution to remove the excess of free mineral acid. Common salt solution was used because the oil, having nearly the same density as distilled water, showed a strong tendency to emulsify if shaken even moderately with water alone.

The separated oil was shaken twice in convenient portions with an excess of 4 *N* sodium hydroxide solution to separate the total tar acids and phenols as water-soluble compounds, and the remaining oil was named for convenience "residual kelp oil."

RESIDUAL KELP OIL—This crude residual oil soon turned dark in the air; its specific gravity was 0.96. A fractionation of 103.7 g. gave results which are typical of the various samples that were distilled. The residue was, after cooling, a thick viscous liquid.

Fractions ° C.	Weight of Oil Grams	Per cent of Oil
90–95	1.9	1.8
220–230	10.8	10.4
235–240	17.8	17.1
250–260	28.0	27.0
270–300	29.4	28.3

The amount of residual oil usually obtained averaged about 20 per cent of the weight of dry tar. Its sulfonation value was 7 to 8 per cent (with 37 *N* sulfuric acid), and the residue was water-white and not affected by strong caustic soda solution. The refractive index of this water-white residue was found to be 1.4660 at room temperature.

Samples of the residual oil and of the crude kelp tar oil were shown by test to be satisfactory flotation oils for ore concentration.

TAR ACIDS—These were separated from the caustic soda solution by acidifying with dilute sulfuric acid and washing out the excess of the mineral acid with a saturated common salt solution. The tar acids thus obtained had a density of 1.024 to 1.041. The yield was found to average 11.1 per cent of the weight of dried tar. They were nearly black in color and cresolic in odor. Di- and triatomic phenols may be present with the cresols and their homologs, as their presence would account for the rapid darkening in color of these acids when they are brought into contact with air. That these so-called tar acids are almost entirely made up of phenolic bodies is shown by the fact that only slight amounts of oily material could be separated by shaking with sodium carbonate solution.

A rectification of this crude phenol (27.1 g.) gave the following results:

Fractions ° C.	Weight of Fractions Grams	Per cent of Oil
209–215	6.5	24.0
215–220	3.3	12.1
220–225	2.8	10.3
225–250	6.4	23.6

The first fraction gave a decided blue color with ferric chloride, indicating the presence of cresols, especially *o*-cresol. No guaiacol was found on careful examination. There was no sulfonation residue.

Under the direction of Mr. E. P. Devlin, of the Forest Products Laboratory, a disinfectant solution was made with the crude tar acids as follows: Mix 45 cc. of residual kelp oil with 15 cc. of tar acids. Dissolve 5 g. of caustic soda in water and add 25 g. of rosin. Warm until dissolved; then evaporate the water from the soap. Add the above oil mixture to the soap, stir until dissolved, and make up to 100 cc. with water.

Samples of crude tar acids, crude residual kelp oil, and the disinfectant made from them according to the above formula, were submitted to the Bureau of Chemistry for a test of their toxic properties. The report from the Bureau of Chemistry follows:

> The sample of crude tar acids and crude kelp oil were non-miscible in water and non-susceptible to Rideal-Walker and Hygienic Laboratory tests for phenol coefficients.
>
> 0.1 cc. of the crude tar acid sample sterilized 10 cc. of culture of *B. typhosus* in 15 min. 0.1 cc. of the same sample failed to sterilize 30 cc. of culture in 1 hr. These mixtures would be 1–100 and 1–300 proportions, respectively. Phenol under like conditions kills *B. typhosus* in 15 min. in 1–100 dilution and fails to kill in 1 hr. in 1–200 dilution. 1 cc. of the crude kelp oil sample killed 4 cc. of culture of *B. typhosus* in 1 hr. It failed to kill in 30 min. 1 cc. failed to kill 9 cc. of culture in 1 hr. The disinfectant from kelp tar was found to have an R.-W. coefficient of between 1.5 and 2.0.

A sample of the disinfectant from kelp tar was also examined by the Pathology Section of the Forest Products Laboratory for its toxic power against *Fomes annosus* Fr., a wood-destroying fungus. The relative toxicities of kelp-tar disinfectant compared with pure coal-tar creosote and zinc chloride may best be summed up in a quotation from an informal report on the work in the files of the Forest Products Laboratory:

> Kelp-tar disinfectant is one and one-fourth times as toxic as pure coal-tar creosote, and twice as toxic as the zinc chloride and gum arabic emulsions of coal-tar creosote. The killing points are 0.25, 0.35, 0.5, and 0.55 per cent, respectively.

TAR BASES—With the exception of ammonia, no bases have been distilled from kelp tar. All tests for pyridine and amino compounds have been negative, whether the supposed bases were removed by steam distillation or by taking up with ether after liberation from the acid solution with caustic alkali. In each case an oily substance of pleasant odor was recovered which appeared to be basic in its properties but, when neutralized with acids, yielded nothing more than a mixture of ammonium salt and an oil. Attempts to make a double compound with platinic chloride were fruitless. It is extremely improbable that nitrogen can be combined to any large extent as ammonium salts in kelp tissue. It is more probably combined in an unstable compound which breaks up readily on heating into ammonia and hydrocarbon derivatives. An attempt was made to isolate a base by treating the acid solution of kelp bases with sodium carbonate solution, thereby avoiding the evolution of ammonia, but no better results followed. The same oil separated, but it did not form stable compounds with acids.

PITCH—The residual pitch from this tar was a black, brittle substance with a nitrogen content of 3.53 per cent; its specific gravity was 1.17, and its melting point was 130° C. When fused with caustic alkali and iron filings a small amount of Prussian blue was recovered. Free carbon was absent.

EXAMINATION OF HIGH-TEMPERATURE TAR

By high-temperature kelp tar is meant the tarry distillate that is formed at temperatures ranging from 800° to 950° C., as produced in the retorts at the Summerland plant.

DISTILLATION APPARATUS—This tar gave so much trouble by frothing that a special distilling apparatus had to be devised to guard against losses by overflowing and to condense the greatest possible amount of oil vapors from the distillate.

A 2 qt. iron retort was heated by a sand bath and the vapors from the hot tar were carried into the flask A, by a current of heated air which was aspirated through the whole system. Flask A was surrounded by hot water, thus permitting the lower boiling vapors to pass on into Flask B, while the heavier oils collected in A. B was a flask surrounded by ice water from which any still uncondensed vapors led into a reflux spiral condenser, thence into a final wash bottle, C. In this way the greater part of the oils were condensed. While a succession of condensers seems to be necessary for the recovery of most of the distillate, the oils collected in different condensers showed nearly the same properties so there was no real separation of the various constituents of the distillate.

Approximately 10 per cent of alcohol intimately mixed with each charge of tar was found to diminish the frothing by reducing the surface tension of the tar bubbles and at the same time carrying off the water. The melted tar was easily miscible with alcohol.

A retort was finally devised at the Summerland kelp plant which contained a perforated disk at the base of the dome. A jet of air under pressure was directed against this disk from above which broke the foam as it came through the perforations. In this way several gallons of tar were successfully distilled at a time.

PROPERTIES OF "THICK" AND "THIN" TARS—The two samples investigated have been referred to as the "thick" and "thin" tars for convenience. The thick tar was collected under such conditions that a large part of its water and some of the volatile oil had already been distilled out by the heat of the furnace. The thin tar was taken directly from the condenser and probably represented the true tarry distillate from kelp better than the other. It is interesting to note that the percentages of volatile oils in each are about the same and, so far as could be learned, the constituents of these oils are nearly identical. The thick tar had a nitrogen content of 4.24 per cent, but the thin tar had only 2.64 per cent of nitrogen.

A description of the first distillation of thick tar is given as typical of the others.

The distillation proceeded slowly but smoothly, owing, no doubt, to the presence of alcohol. Alcohol commenced to come over at 85°. The air condenser was not connected until the temperature had risen to 100°. After 105° had been passed, the flame was carefully increased from time to time. Above 115° the distillate became a yellow oil. At 120° some tar froth seems to have been carried over, the flame was decreased, and the distillation continued. At 130° to 153° the distillate reacted strongly alkaline, and at 240° it was a thick dark-brown semi-solid, while above 255° it became limpid and lighter colored.

TABLE II—DISTILLATION DATA ON THICK KELP TAR

Weight of Sample G.	Alcohol Cc.	Fract. 100°–150° G.	Fract. 150°–200° G.	Fract. 200°–280° G.	Total G.	Total Per cent	Pitch G.	Pitch Per cent
314	42	21	1	44	66	21.0	194	61.7
690	60	92	31	29	152	22.0	401	58.1
673	70	62	14	..	131	19.4	433	64.3
668	70	114	..	..	114	17.0	462	69.1
641	70	138	14	..	152	23.7	403	62.8

Distillates A and B showed specific gravities of 0.989 and 0.986, respectively, at 20° C., and their composition must be similar also, because on shaking successively with acid and alkali A yielded 69.5 per cent of residual oils and 25.7 per cent of phenols, while B yielded 72.3 per cent of residual oil and 22.8 per cent of phenols. The corresponding oils from A and B were accordingly mixed for further treatment.

TABLE III—DISTILLATION DATA ON THIN KELP TAR

Weight of Sample	Dist. A		Dist. B		Pitch	
G.	G.	Per cent	G.	Per cent	G.	Per cent
1002	174.0	17.3	29.5	2.9	367.0	36.6
1096	114.5	14.5	102.5	9.3	352.0	32.1
1172	158.5	13.5	87.5	7.4	404.5	34.5
1232	108.5	8.8	50.0	4.0	395.3	32.0

As has been stated, it was hoped that the distillation of such a nitrogenous body as dried kelp at the temperatures employed in coal distillations might possibly yield a tar that would be similar in many ways to coal tar and furnish some of the highly desirable hydrocarbons that are obtainable from coal tar. So far as known, kelp has never before been distilled on a large scale, *i. e.*, in ton lots, so the possibilities have heretofore been a matter of conjecture only. With the exception of phenolic substances, however, none of the well-known compounds of the coal-tar distillation have yet been recognized.

PITCH—The residual pitch from the tar distillation apparently has little value as pitch, but its nitrogen content runs from 3.5 to 5.15 per cent and this nitrogen is in such a form as to permit the preparation of Prussian blue by fusion of the pitch with iron turnings and caustic alkali in an iron crucible. The yield of pigment is very small, but it must be remembered that only a small amount of nitrogen is ever recovered as cyanide by this process. If the pitch should ever be prepared in large quantities the production of Prussian blue might assume great importance as a kelp by-product. Kelp pitch is a brittle substance with a specific gravity of 1.17, and melts at 130°. There was little, if any, free carbon in the samples that were tested.

EXTRACTION OF DISTILLATES WITH ACID AND ALKALI—The manipulation of this oil with acid and alkali is by no means simple, as the oil has a great tendency to emulsify and the resulting foam is broken up only with considerable difficulty. Slow and careful mixing is the only way to prevent this trouble.

The best strength of acid and alkali for this work was found to be approximately 4 *N*. Sulfuric acid and caustic soda were always used but an experiment showed that hydrochloric acid of equivalent strength served equally well and had the same solvent action on the acid-soluble oil which has already been mentioned under low-temperature tars as separating with the ammonia.

The procedure in handling the oily distillates was to effect the separation of neutral oil and phenolic substances by shaking out with acid and caustic soda, then to rectify each of the products by distillation. The first extractions with acid and alkali were never complete and it was necessary to distil the resulting oils and once more to shake out these distillates with acid and alkali.

The first distillates from tar were far from being uniform mixtures, hence the percentages of phenols and residual oils varied after the extractions of these distillates with acid and alkali. For example, four of these extractions of an oil that had been collected in Flask A varied among themselves as indicated in the following table. Oils collected in Flask B also varied to some extent.

Flask	Residual Oil Per cent	Phenols Per cent
A	76.9	15.3
	83.0	15.0
	63.0	13.5
	73.1	10.2
B	73.1	20.3
	72.3	22.8

Such figures as the above are by no means accurate for the reason that some of the aqueous solution is taken up by the oil in an emulsion that is impossible to break up by any means except distillation. The oil also contains water-soluble constituents. In one case 54.0 g. of oil were shaken successively with two 20-cc. portions of distilled water. The weight of residue after evaporating the water was 2 g.

DISTILLATION OF RESIDUAL OIL FROM FLASK A—When a sample of 217 g. of the residual oil in Flask A was heated with a free flame to 120°, a mixture of oil and water distilled over. The oil was separated from the water, returned to the distilling flask, and the distillation resumed. The residue was rejected. Each fraction turned dark red on exposure to air.

Fractions	Grams	Per cent
120°–190°	6.0	2.7
190°–250°	87.0	40.0
250°–296°	68.0	31.3
Total	161.0	74.0

TREATMENT OF FRACTIONS—*Distillate 120°–190°:* 6 g. shaken out with sulfuric acid and alkali. The greater part of the oil was soluble.

Distillate 190°–250°: 87 g., treated as above.

	Grams	Per cent
Neutral oil	63.0	72.4
Phenols	21.8	25.0

Distillate 250°–296°: 68 g., treated as above.

	Grams	Per cent
Neutral oil	55.5	81.6
Phenols	6.2	9.1

A dark oil separated when the sulfuric acid extract was neutralized but there was no odor of ammonia.

The total neutral oil recovered amounts to 54.6 per cent of the crude oil distilled from tar and to 7.6 per cent of the original tar itself. Likewise the phenols are only 15.7 per cent of the crude oil and 2.2 per cent of the tar.

DISTILLATION OF CRUDE PHENOLS—The crude phenolic acids were purified by distilling and afterwards shaking out the fractions with caustic soda solution.

Fractions	Grams	Per cent
150°–180°	4.4	2.06
180°–215°	33.5	15.7
215°–260°	79.6	37.3

Fraction 150°–180° (4.4 g.) was shaken with 11 cc. of 4 *N* NaOH.

	Grams
Insoluble oil	0.7
Phenols recovered	2.7
Soluble residue	1.0

Fraction 180°–215° (33.5 g.) was shaken with 77.5 cc. NaOH.

	Grams
Insoluble oil	2.4
Phenols recovered	29.0
Soluble residue	2.11

Fraction 215°–260° (79.6 g.) was shaken with 184 cc. of the alkali.

	Grams
Insoluble oil	5.2
Phenols recovered	74.8
Soluble residue	None

	Grams	Per cent
Total phenols finally separated	106.5	50.0
Insoluble oils	8.3	
Soluble residues	3.1	
Total	117.9	

The separated phenols were finally all mixed and 61.7 g. were redistilled.

Fractions	Weight of Fractions Grams	Per cent of Oil
150°–215°	23.6	38.2 (24.0)
215°–220°	8.1	13.1 (12.1)
220°–240°	15.0	24.3 (33.9)

The numbers enclosed in parentheses are corresponding percentages of distillate from the tar acids made at temperatures ranging from 480° to 650° (p. 788). The higher kelp distillation temperatures seem to produce more phenols of cresolic nature than the lower temperatures.

Likewise a comparison of the residual oils of the tar produced at 480° to 650° C. with the high-temperature tar can best be made by observing the distillation fractions of corresponding temperature ranges as set forth in the following table:

Distillation Fractions	Tar 480°–650° Per cent	Tar 800°–950° Per cent			
		Per cent	Per cent	Per cent	Per cent
220°–250°	27.5	47.4	40.0	58.6	68.1
250°–300°	55.3	21.4	31.3	20.7	16.3

The results indicate that the high-temperature distillation of kelp produces a larger amount of low-boiling oils than the lower temperature distillation does.

FRACTIONATION OF THE RESIDUAL OIL FROM KELP TAR

It is unnecessary to take up the repeated rectifications of the residual kelp oil that were necessary to secure working material for analysis and further investigation. The final results of the fractionation at atmospheric pressure, together with the densities of the distillates, are set forth in the following table:

Fractions ° C.	Weights Grams	Densities 20° C.
175–200	58.9	0.9306
200–210	45.3	0.9454
210–220	58.6	0.9517 over sodium
220–230	48.0	0.9522 over sodium
230–240	55.6	0.9958 over sodium
240–250	28.2	....
250–260	100.6	0.9620
260–270	54.1	0.9700
270–280	28.4	0.9750

It was noticed that all reacted with sodium as long as the metal lasted. The higher boiling fractions seemed to react more vigorously than the lower boiling fractions.

Fractions 210°–220° and 220°–230° had so nearly the same specific gravities that they were combined and finally rectified by distillation in a vacuum. The oil showed great tendency to froth when distilled in vacuum, and this property seems to be common to all kelp distillates. It is evident from the above fractionation table that this substance is a mixture possibly of many oils of different boiling points. The steady rise in temperature during the entire process of rectifying the crude residual oil is a rather discouraging indication that individual compounds can be isolated only with much difficulty and in small yields.

The product of the first vacuum distillation came over between 74° and 80° C. at 5 mm. pressure. It was pale yellow in color when fresh but turned darker on standing. Density 0.9524 at 20°; refractive index 1.4972 at room temperature. The oil showed no optical rotation.

The distillate thus prepared (weighing 77.7 g.) was further purified by shaking in a separatory funnel with 40 cc. of 5 per cent sodium hydroxide solution. After washing with water the oil was next shaken with 15 cc. of saturated sodium thiosulfate solution and once more washed with water. It should be remarked here that the oil still showed a tendency to emulsify if shaken too violently, also it was noticeable that the wash water was slightly colored after being shaken with the oil. Under these circumstances, too, the oil became sticky and adhered to the glass walls of the funnel, which made a good separation from water more difficult. The oil was dried over anhydrous sodium sulfate and transferred to a distilling flask from which it was finally distilled over metallic sodium in a vacuum of 3 mm. During the distillation the oil required much care to keep down spurting. The main distillate came over between 73° and 80° C. and was immediately analyzed by combustion. Any formula that might be derived from this analysis has no significance because subsequent treatment with bromine showed the oil to be still a mixture.

Weight taken, 0.1560 g. Weight of carbon dioxide, 0.4730 g. Weight of water, 0.1299 g.

	Found Per cent
C	82.7
H	9.2

Another fraction, 250°–260°, was also rectified *in vacuo*. The first drop came over at 91° at 18 mm. pressure and the following fractions were collected:

Fractions	Grams
91°–112°	2.7
112°–121°	27.0
121°–132°	26.3
132°–136°	8.4

Fraction 112°–121° was analyzed by combustion.

Weight taken, 0.1548 g. Weight of carbon dioxide, 0.4678 g. Weight of water, 0.1300 g.

	Found Per cent
C	82.4
H	9.3

This analysis shows a close agreement with that of the distillate just described. Bromination in ether solution, however, showed that both fractions are mixtures of at least two different compounds.

Five grams of the 73° to 80° distillate were dissolved in 20 cc. ether and 5.5 g. of bromine added from a buret while keeping the ether solution cooled by ice water. A dark, heavy oil immediately settled out and the ether solution was colored slightly red. The ether was decanted from the heavy oil and the solvent driven out by a blast of air, leaving a residual oil which was next washed with sodium carbonate solution to remove free hydrobromic acid, etc. Weight of ether-insoluble oil remaining, 1.8 g.; of ether-soluble oil, 6.5 g.

The ether-insoluble oil is very smeary and gives no promise of being a satisfactory working material. The ether-soluble oil, however, is more promising. When a small quantity was heated in a test tube there were indications of decomposition, so the oil was first subjected to a steam distillation. Five grams of oil were weighed into a flask and 10 cc. alcohol added. During the steam distillation a pale yellow oil with a sharp odor came over. When distilled at atmospheric pressure a nearly colorless oil was obtained which boiled between 210° and 220°. There was some indication of decomposition, showing that only vacuum distillations should be employed.

AQUEOUS DISTILLATE FROM KELP

This distillate corresponds to the so-called "ammonia liquor" from coal-gas retorts. It is an amber-colored solution of ammonium salts and organic matter. The liquid usually reacts alkaline to litmus, but not in every case.

Its specific gravity ranges from 1.01 in the first runnings to 1.065 in the later distillates. These aqueous products, as made in the oil-jacketed retort in the Forest Products Laboratory, were always acid to litmus paper, but those made at higher temperatures were always alkaline. The acidity was never established because, as the end-point was approached in titration, the solution became so turbid that it was impossible to make out when neutrality was reached.

When kelp was heated in a wood retort to the temperature to which wood is subjected in distillation, there were many marked differences in the behavior of the two substances. With wood an exothermic reaction sets in at about 230° and the heat of this reaction often raises the temperature to 400°, while with kelp there was no appreciable exothermic action. The greater part of the alcohol and acetic acid are formed, in the case of wood, during this spontaneous decomposition, and as there appears to be no corresponding breaking up of cellular tissue in kelp distillation, one can hardly suppose that any appreciable quantity of methyl alcohol and acetic acid is produced under such conditions.[1]

The residue, on evaporation of 10 cc. of the aqueous liquor, varied according to the temperature employed in the distillation. The residues from the low-temperature distillations at the Forest Products Laboratory averaged 9.33 g. per 100 cc., while those obtained from the liquors produced at Summerland ranged from 3.66 g. to 7.93 g. per 100 cc. The condensation of the distillate in the wood-distilling retort was very complete, but in the large retorts of the government plant there was much greater opportunity for the escape of steam and of substances volatile with steam.

The ammonia content of the low-temperature distillate averaged 0.32 per cent of NH_3, which corresponds to a 1.7 oz. ammonia liquor, *i. e.*, one gallon of the liquor would furnish 1.7 oz. of ammonium sulfate.

The kelp liquor made in Summerland at high temperature, however, always smelled of ammonia. One sample was found to contain 0.76 per cent NH_3, which corresponds to a 4 oz. gas liquor. Such a liquor is well worth working up for ammonia recovery.

The residue, after evaporation of this aqueous distillate, is a pasty, amber-colored substance with a faint odor, and is a mixture of compounds including ammonium salts.

When 109.7 g. of this substance were distilled on a sand bath a small amount of water mixed with a few drops of a very evil-smelling oil and some ammonia first came over at 104°. After this the temperature rose rapidly to over 200° and the principal distillate followed.

The principal fraction (275°–285°) was a liquid of reddish color with a strong green fluorescence, and somewhat less viscous than glycerol. It was soluble in water and alcohol and had a slightly astringent burning taste. Its water solution was mildly alkaline to litmus paper and decidedly so to methyl orange, but a qualitative test for nitrogen was negative. The specific gravity at 23° was 1.3431 and the refractive index was 1.5013 at 28°. There was no optical rotation.

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[1] D. R. Hoagland, "Study of the Organic Constituents of Pacific Coast Kelps," *J. Agr. Res.*, **1**, 39.

Temperature ° C.	Products Grams
104–186	4.6
186–275	9.0
275–285	59.5
285–295	19.5

The fluorescence disappeared on dilution with water; hence it must have been due to slight amounts of foreign substances. When chilled in a freezing mixture of ice and salt the liquid showed no tendency to solidify. Several unsuccessful attempts were made to form an acetyl derivative with acetic anhydride.

When distilled in a vacuum there was at first a great tendency to frothing, so that a 500 cc. distilling flask was needed to prevent the liquid from being carried over with the vapors. The final rectification of these distillates was made in a 4 mm. vacuum. The weight taken was 80 g. Distillation commenced at 75° but most of the distillate came over at 125°. The amount collected was 65.9 g., or 82.3 per cent. The distillate finally obtained was a straw-colored liquid which distilled between 109° and 113° at 2 mm.

An analysis by combustion gave the following results:

Weight taken, 0.2107 g. Weight of carbon dioxide, 0.3668 g. Weight of water, 0.1318 g.

	Found Per cent	Calculated for $C_{10}H_{16}O_6$ Per cent
C	50.3	51.7
H	7.0	6.9

Considerable work is necessary to identify this material fully, but it is undoubtedly a hydroxyl compound of the glycol or glycerol series. This belief is supported by the fact that it liberates hydrogen gas when treated with sodium. Its close resemblance to glycerol in physical properties indicates that it could doubtless be recovered from the aqueous kelp distillate in the ordinary distilling apparatus used for the recovery of glycerol from soap liquors, and it might be of value as a glycerol substitute for mechanical purposes.

SUMMARY

In the foregoing account it has been shown that kelp tar can be separated into groups of compounds which may be designated tar acids, neutral oils, ammonia, and pitch. These groups have been studied and their general characteristics determined, although the chemical identity of the constituent compounds has not been established.

The crude kelp creosote has a high toxicity and the residual kelp oil has value as a flotation oil. These products would find a ready market. The pitch residue from kelp-tar distillation is a source of nitrogen for Prussian blue and cyanogen compounds.

The aqueous kelp liquor contains ammonia in workable quantities and the water-soluble distillate from the residue on evaporation might be used as a glycerol substitute for mechanical purposes.

ACKNOWLEDGMENT

Full acknowledgment is here made to the officials of the Forest Products Laboratory for the use of space and apparatus, and for courtesies extended; likewise to Prof. E. B. Fred, of the University of Wisconsin, for use of laboratory space and apparatus.

THE TESTING OF SACCHARIMETERS BY MEANS OF THE TELESCOPIC CONTROL TUBE[1]

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A graduated telescopic polarization tube in saccharimetric analysis was first used by Jellet[2] in 1864. Although it possesses applications which greatly simplify certain problems of analysis, the possibilities of this ingenious instrument have been generally overlooked. In 1884, just twenty years after the publication of Jellet's paper, Schmidt and Haensch[3] described a telescopic observation tube for controlling the accuracy of their saccharimeters, to which they gave the name of "Control Observation Tube."

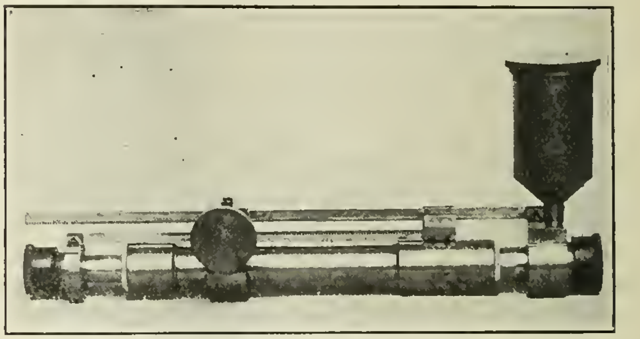

Fig. 1—Telescopic Control Tube

The control tube, as manufactured by Schmidt and Haensch and as described by Landolt[4] in his classic work upon "Optical Rotation," consists of a telescopic metal tube (Fig. 1) which can be adjusted by means of a screw to give a column of solution for any length between 225 mm. and 410 mm. By means of a vernier the exact length of solution at any point within this range can be read upon the scale to 0.1 mm.

Before using the control tube it is important that its scale be accurately verified. The tube employed in the present work showed by the Landolt gage, at the time of purchase, an error of about 0.2 mm. at all points of the scale. A more accurate calibration by the Bureau of Standards showed errors ranging from 0.15 mm. at the 410 point of the tube scale to 0.24 mm. at the 230 point.

The control tube has been subjected constantly to a number of uses in the work of this laboratory during the past ten years. It has been employed: (1) for determining the errors of saccharimeter scales due to optical impurities in the quartz wedges or to inaccuracies in marking the scale divisions, (2) for comparing the scales of different saccharimeters, (3) for determining the comparative accuracy of reading, or sensibility, of different saccharimeters, (4) for testing the ability of new assistants to read the saccharimeter accurately, and (5) for determining the influence of the personal equation in saccharimetric observations.

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[1] Read before the Sugar Section at the 59th Meeting of the American Chemical Society, St. Louis, Mo , April 12 to 16, 1920.

[2] *Proc. Roy. Irish Acad.*, **8** (1864), 279.

[3] *Z. Instrumentenk.*, **4** (1884), 169.

[4] "Das Optische Drehungsvermögen," 2nd Ed., **1898**, p. 398.

One great advantage of the control tube for these various purposes is that it eliminates completely the influence of bias, by which we mean the unconscious inclination of an observer, more especially of the inexperienced, to find an expected reading. If a standardized quartz plate, for example, is marked 96.2, an observer will unconsciously strive to read it 96.2; whereas with the control tube, whose readings are in millimeters instead of in sugar degrees, the measurements mean nothing until after the experiment is finished and the final average of the series is calculated into its scale equivalent.

(1) USE OF THE CONTROL TUBE FOR DETERMINING THE ERRORS OF SACCHARIMETER SCALES

This is the chief purpose for which the control tube was designed and the principle of its application is familiar. Assuming that the wedges are perfectly constructed of optically pure quartz, that the dividing engine of the manufacturer has made no error in marking the scale divisions, and that the observer has the necessary accuracy of eye to set the zero of his vernier exactly with any desired scale division, the length of sugar solution necessary to read 90° should be exactly 90 per cent of the length necessary to read 100°, and so for the other divisions. The extent of the divergence of any division from its marked value is the scale correction for that particular division.

In beginning an experiment the operator first makes certain by a series of careful readings that the zero point of his instrument is in perfect adjustment, and then places in the trough of the saccharimeter the control tube which has been filled with a perfectly clear solution containing about 25.5 g. of refined sugar in 200 cc. The temperature should be kept as constant as possible in the neighborhood of 20° C. The polarization cabinet should be well ventilated by an electric fan to carry away the heat given off by the observer. There will, however, always be a slight amount of warmth imparted to the tube and its contents through the constant contact of the observer's hand with the adjusting screw. A warmer sugar solution requires a greater tube length for compensation. It is highly important, therefore, that the errors due to heat transmission, to eye fatigue, to the slight evaporation of water from the joints of the tube (which for easy operation cannot be made perfectly airtight) and to other causes should be evenly distributed. This is accomplished by making one tube reading at a time for each scale division proceeding from the 100° point to the 95th division, and so on for every fifth division to the 55° point, which is the last division for a solution of the given concentration. From the 55th division the observer then retraces his path by 5 degree stages back to the 100° point. For a set of ten readings the tube would thus be alternately shortened and lengthened ten times. The completion of a set of ten readings for ten points of the scale requires about an hour. On the following day the verification is repeated with a fresh tube of solution, it being necessary for accuracy that the tube be emptied, washed, and dried after each experiment. The average length of tube for each scale division is then corrected for the error in the tube scale; the corrected tube length found for each division of the saccharimeter scale multiplied by 100 and divided by the corrected tube length for the 100° point of the saccharimeter scale gives the determined value of that division. Thus if the value 89.9 be found for the 90° point it means that all saccharimeter readings in the neighborhood of the 90° point should be corrected by subtracting 0.1.

The two saccharimeters employed in the work of this laboratory have been tested annually by four observers in the manner just described over a period of eight years. As each observer makes two sets of ten readings there are eighty in each yearly average and 640 readings in the total average for each of the scale points tested. There are probably few, if any, other saccharimeters in existence whose scales have been more carefully scrutinized.

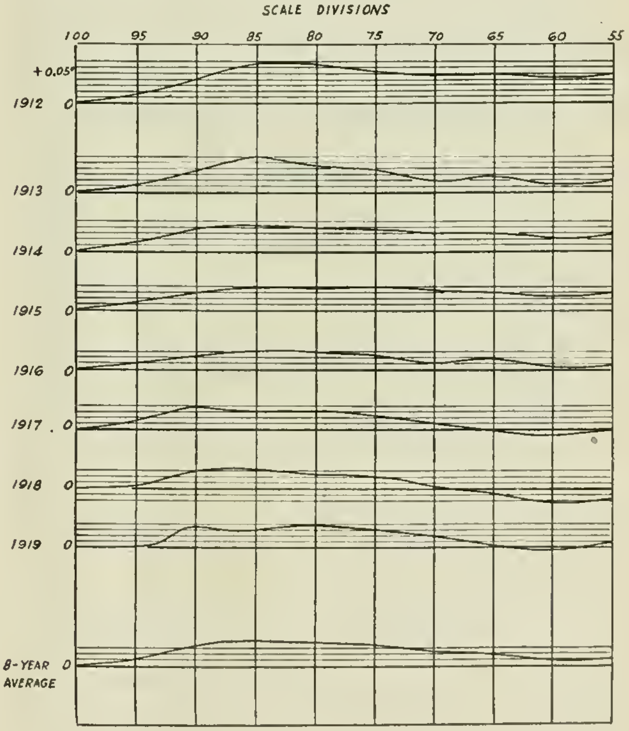

FIG. 2—CORRECTION CURVES. SCHMIDT-HAENSCH SACCHARIMETER No. 6920

The correction curves for the scales of the two saccharimeters, which are, respectively, double-wedge instruments of the Schmidt-Haensch and Fric[1] types, are given in the accompanying diagrams. The curves are necessarily much compressed. The vertical coordinates of scale correction are in hundredths of a degree and the horizontal coördinates, to have the same ratio, would need to be magnified fifty times. The minor irregularities of the annual curves disappear in the final average, the plus errors of one curve being counterbalanced by minus errors of another. The dominant irregularities peculiar to each scale are seen in all the yearly curves and make up the final average.

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[1] The Fric saccharimeter was of the U. S. Bureau of Standards type with the Bates adjustment for securing variable brightness of the field (Bureau of Standards, *Bull.* 4, 461).

The curve of the Schmidt-Haensch scale (Fig. 2) requires an additive correction. It rises gradually from the 100° point to the 85th division where it acquires a maximum amplitude of about 0.04 degree and then falls evenly to the 60th division where it has an amplitude of about 0.01 degree; from the 60th to the 55th division there is a slight but unmistakable rise of about 0.006 degree. This slight rise appears in each of the yearly curves, having an amplitude, respectively, of 0.005, 0.006, 0.004, 0.003, 0.002, 0.009, 0.005, and 0.013 degree. This illustrates very well how a constant slight irregularity of less than 0.01 degree, smaller than a single reading can detect, invariably appears in a large average of polarizations. The average correction for any point between the 100th and 55th divisions is +0.0234.

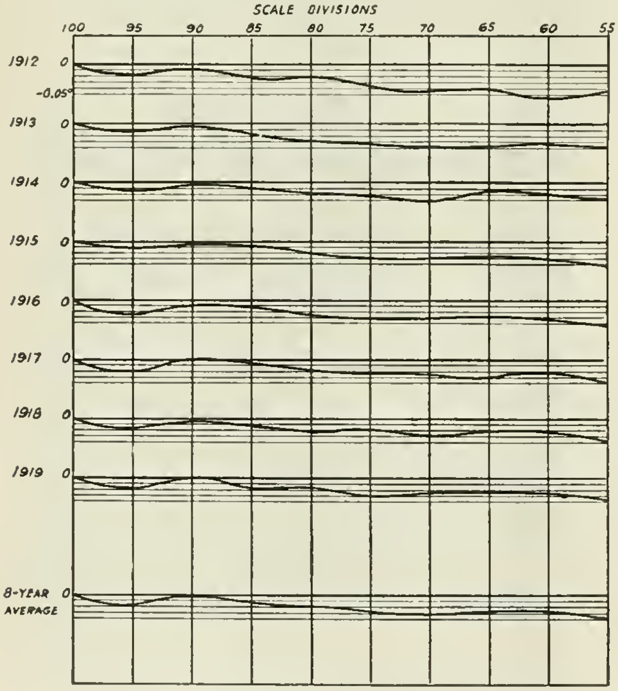

Fig. 3—Correction Curves. Fric Saccharimeter (Bates Type) No. 888

The curve of the Fric scale (Fig. 3) is entirely different from that just described and requires a subtractive correction. There is first a drop of 0.015 degree from the 100th to the 95th division; then a slight rise of about 0.01 degree to the 90th division, which is followed by another gradual drop to the 70th division where the correction is about 0.03 degree; there is then a slight rise of about 0.004 degree to the 65th division, after which there is a third drop to the 55th division where the maximum correction of 0.038 degree is reached. We notice in this, as in the previous set of curves, the persisting effect of small constant influences. The average correction of the Fric scale for any point between the 100th and 55th divisions is —0.0210.

While the general contour of the curves in each set is similar it will be noted in several instances that the amplitudes of a particular curve may be higher or lower than the average. This, of course, is due to slight variations of measurement in the tube length for the basic 100° point which, being used as the divisor of all the other measurements, affects the amplitudes for the whole curve. As previously stated, such variations eliminate one another in a general average.

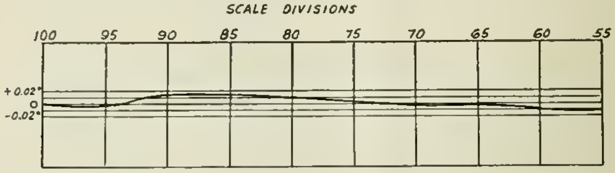

Fig. 4—Composite Correction Curve of Schmidt-Haensch Saccharimeter No. 6920 and Fric Saccharimeter No. 888. Eight-Year Average

In the Schmidt-Haensch saccharimeter there would seem to be a slight progressive decrease from year to year in the scale error. Whether or not a quartz wedge after cutting may undergo a long period of readjustment from some local strain with a consequent slight progressive change in its polarizing power is a question. The Lippich half-prism of this saccharimeter underwent disruption in 1915 and again in 1917, and each time had to be replaced with a new prism. A shifting of the quartz wedge by several tenths of a degree was necessary after each replacement in order to correct the change in zero point, but a movement of the wedge to this slight extent would not affect materially the magnitude of the scale corrections.

The maximum correction for each scale between the 100th and 55th divisions is 0.04 degree. In the case of a new American saccharimeter made by Bausch and Lomb the results of 70 measurements by three observers showed a maximum correction of 0.04 degree for the 60th scale division. The maximum error on all three instruments is well within the 0.05° limit prescribed in the specifications of the American Sugar Chemists.[1] Unless the supplies of optically pure quartz for wedges become depleted, the scales of commercial saccharimeters should without doubt be held within this requirement.

The composite correction curve of the Schmidt-Haensch and Fric instruments is given in Fig. 4. The maximum corrections are +0.014 at the 85th division and —0.012 at the 55th division. The plus and minus corrections on this composite curve very nearly compensate one another, the average correction per division being only +0.0012. It is doubtful if any two saccharimeters could be found which balance each other more exactly. As previously stated, it is upon these two saccharimeters that duplicate polarizations are made of each sample of sugar tested in our laboratory. Over 95 per cent of the polarizations fall between 93 and 100 degrees, and within this limit the composite curve falls almost exactly upon the zero line and no corrections of readings for scale errors have to be applied. The mean values of the scale divisions of the two saccharimeters for the points tested are as follows:

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[1] See report of the committee to formulate specifications for the construction of a polariscope for laboratory use, This Journal, **12** (1920), 440.

	95	90	85	80	75	70	65	60	55
Schmidt-Haensch	95.011	90.033	85.041	80.038	75.033	70.022	65.018	60.009	55.015
Fric......	94.984	89.996	84.988	79.981	74.973	69.970	64.973	59.969	54.962
AVERAGE..	94.997	90.014	85.014	80.009	75.003	69.996	64.996	59.989	54.988

(II) USE OF THE CONTROL TUBE FOR COMPARING THE SCALES OF DIFFERENT SACCHARIMETERS

The comparison of scales of different saccharimeters is made by the control tube in the following way: The zero points of the instruments to be compared are first brought into perfect adjustment. Then the zero of each vernier is set exactly at the 100 point of its scale and the control tube is read in succession upon each instrument until the requisite number of readings by different observers is made. A comparison of the averages obtained by this method upon two saccharimeters is given under Section V.

(III) USE OF THE CONTROL TUBE FOR DETERMINING THE COMPARATIVE ACCURACY OF READING DIFFERENT SACCHARIMETERS

A comparison of the probable errors obtained in a long series of observations with the control tube gives a very accurate means of determining the comparative accuracy of reading different saccharimeters. In the case of the Schmidt-Haensch and Fric saccharimeters the probable errors of the final average of the 640 readings at six scale points were found to be as follows:

Scale Division	Schmidt-Haensch	Fric	Average
95........................	±0.0014	±0.0011	
90........................	±0.0014	±0.0007	
85........................	±0.0027	±0.0011	
80........................	±0.0018	±0.0009	
75........................	±0.0021	±0.0015	
70........................	±0.0028	±0.0015	
Probable error, 640 readings.......	±0.0020	±0.0011	±0.0016
Probable error, one reading........	±0.0514	±0.0286	±0.0400

The average probable error of ±0.04 for a single reading upon the two saccharimeters is the same as that given by the writer[1] in 1914, and is identical with the value reported by Schönrock[2] in 1904.

It will be noted that the accuracy of reading the Fric saccharimeter is nearly double that of the Schmidt-Haensch instrument. There are two explanations for this. The first is that the scale of the Fric instrument, being ruled upon ground glass and read by transmitted light, gives a much greater accuracy in reading than is possible with a metal scale illuminated by reflected light such as that of the Schmidt-Haensch saccharimeter. Schönrock gives the error in reading the vernier of a saccharimeter scale as ±0.02 sugar degree, but such a deviation can easily be detected on the Fric scale. The second explanation for the higher accuracy in reading the Fric saccharimeter is that the adjustment of the half-shadow angle by the mechanism of Bates to the point of maximum sensibility gives a greater accuracy in setting the field. The fixed half-shadow angle of the Schmidt-Haensch saccharimeter was about 7 angular degrees, which is a little too large for colorless solutions, although about right for the average class of raw products.

(IV) USE OF THE CONTROL TUBE FOR DETERMINING THE PROBABLE ERROR OF THOSE WHO READ THE SACCHARIMETER

The method of determining the probable error of an observer by the control tube requires but a brief description. It is useful in testing the ability of new assistants and consists in having the observer take a large number of tube readings for several points of the saccharimeter scale. The measurements are compared, the variations of each reading from the average determined, and the probable error calculated in the usual way.

(V) USE OF THE CONTROL TUBE FOR DETERMINING THE INFLUENCE OF PERSONAL EQUATION

It is a commonly observed fact that in a given group of chemists certain ones tend always to read sugar solutions upon a saccharimeter higher and others always lower than the general average. These individual variations are largely due, as Landolt, Schönrock and others have pointed out, to the fact that all the rays of white light are not rotated in a saccharimeter by the sugar solution and quartz compensation to exactly the same degree, the consequence being that the two halves of the field show a slight difference in color at the end-point. The varying sensibility of different observers to this inequality in color—owing to differences in eye pigment, to variations in sensitiveness of the retina or to other physiological causes—produces one-way divergences in reading. It is for this reason, as Landolt[1] points out, that "exact measurements can never be made with a saccharimeter without perceptible systemic errors." The extent of these physiological variations has been reduced by the employment of a bichromate light filter which removes the most disturbing light waves of shortest wave length. But bichromate-filtered white light is far from being monochromatic and the disturbances due to difference in rotation dispersion are still pronounced. Schönrock[2] noticed between different observers variations in the polarization of sugar solutions of 0.145 degree when using unfiltered white light. By using bichromate-filtered white light these variations were reduced to 0.047 degree or to about one-third. Constant one-way variations of this magnitude can in fact be easily demonstrated by the control tube.

A comparison between different observers in this laboratory during a period of eight years shows that on the same instrument the order of each observer, according to the magnitude of control tube measurements, is always the same. But in correlating the readings of these observers on different instruments the interesting fact was noted that the order of observers on the Fric saccharimeter was exactly the reverse of that found on the Schmidt-Haensch, the chemist who read highest on one instrument always reading lowest on the other. This is shown for example in the following averages for tube readings at the 100° points of the two instruments. The readings were made alternately, Observer A reading the S.-H. instrument, then B the Fric, then C the S.-H., then A the Fric, and so on, until thirty readings had been taken on each instrument.

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[1] *Louisiana Planter*, **54** (1915), 30.
[2] *Z. Ver. Zuckerind.*, **54** (1904), 521.

[1] *Loc. cit.*, p. 378.
[2] *Loc. cit.*

OBSERVER	Schmidt-Haensch Mm.	Fric Mm.	Average Mm.
A	409.170	408.970	409.070
B	409.055	409.145	409.100
C	409.035	409.160	409.098
AVERAGE	409.087	409.092	409.0895

Dividing the above results by the general average 409.0895 gives the following values in terms of the saccharimeter scale.

OBSERVER	Schmidt-Haensch	Fric	Average
A	100.020	99.971	99.9955
B	99.992	100.013	100.0025
C	99.987	100.017	100.0020
AVERAGE	99.9997	100.0003	100.0000

It will be noted that there is a difference of about 0.04 degree between Observers A and C, although the general averages for each observer on different instruments and of all observers on one instrument are in good agreement.

The reversal of the personal equation order upon the two instruments suggests at once that there must be some reversal in the placement of their optical parts, and such indeed is the case. In the Fric saccharimeter the Lippich half-prism is upon the right, and in the Schmidt-Haensch saccharimeter upon the left of the field. Whether or not there are other differences in construction which may explain the reversal[1] of personal equation is not known. The fact, however, remains that the type and construction of polarizer and other details peculiar to each individual saccharimeter have much to do with the personal equation of the observer.

Schönrock[2] discusses the difference in reflection and absorption of the rays of different wave lengths by the Lippich half-prism and the disturbing effects due to this cause would, of course, be shifted from one side of the field to the other by changing the position of the prism. In the Lippich triple field these disturbances would be balanced, and this is no doubt one explanation of the increased accuracy of the Lippich triple-field instrument.

The foregoing table shows a difference of 0.049, 0.021, and 0.030 degrees, respectively, between the readings of each observer on the two saccharimeters. These differences are considerable and they emphasize the caution that is necessary in making comparisons for what is true of one individual is not necessarily true of another. The average of the observations of A, B, and C in the previous table is true only for them, and for another set of three observers where the individuals happened to be all of type A or of type C different values would be obtained; the observers of type A, for example, all reporting that a normal weight of sucrose polarizes 0.05 higher upon the Schmidt-Haensch saccharimeter than upon the Fric instrument, and those of type C that it polarizes 0.03 lower.

The relative value of the disturbances due to unequal reflection and absorption of the different rays of white light in the half-prism of the polarizer, to unequal rotation of these rays by the sugar solution and quartz compensation and to other causes is a question which we cannot answer. We will only point out that the sum of these influences, whatever their relative value, is not proportionately the same at all parts of the saccharimeter scale. If each personal equation had a value of X for a reading of 100 and a value of 0.9X for a reading of 90, and so on, the disturbances having the same proportionate weight in divisor and dividend should not affect the quotients which are calculated from the readings of the control tube. But the results show that these disturbances do affect the calculations from the readings of the control tube from which we must conclude that the sum of the disturbing factors does not descend in a straight line from its value at 100 degrees to nothing at zero degrees.

The following table gives the average results of 100 observations on the control tube for four different observers at the 90° and 80° points:

OBSERVER	Schmidt-Haensch 90°	Schmidt-Haensch 80°	Fric 90°	Fric 80°
A	90.041	80.051	89.987	79.971
B	90.032	80.031	89.993	79.974
C	90.027	80.028	89.997	79.988
D	90.026	80.021	90.007	79.995

The order of the observers is the same for all the determinations upon one instrument but is exactly the reverse when the polarizations are made upon the other instrument. The results show that personal equation may produce differences of as much as 0.03 in testing saccharimeters by the control tube, which leads us to the conclusion that where this means of verification is employed each set of observers should perform its own calibration.

The leading conclusion which we would draw from the testing of saccharimetrs by the control tube is the one expressed by Landolt, over twenty years ago, that the quartz wedge saccharimeter, even in its most highly perfected form, contains certain inherent defects which prevent it from ever becoming an instrument of the highest precision. A saccharimeter upon which every observer can obtain exactly the same reading of a sugar solution is an impossibility. It is not surprising, therefore, that disputes should arise from time to time about the correctness of normal weights, and they will continue to arise as long as each saccharimeter and each human eye retains its peculiar individual characteristics. From the observations of as many individuals as possible a mean value for a normal weight can be calculated which will be generally correct for the average eye but deviations from this value of several hundredths of a degree in individual cases can always be expected, until a delicate impersonal photometric method can be devised for matching the two halves of the field.

In conclusion the author desires to acknowledge the help received from his assistants, Messrs. C. A. Gamble, G. H. Hardin, and M. H. Wiley, in the experimental work of this paper.

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[1] Dr. W. D. Horne has mentioned to the author a similar experience of reversal of personal equation produced by setting the field of the saccharimeter with the head bent downward or by looking at the image of the field in a mirror.

[2] *Loc. cit.*

SOME IMPROVEMENTS ON THE NEEDLE TYPE THERMOCOUPLE FOR LOW TEMPERATURE WORK[1]

By George F. Taylor

Bureau of Plant Industry, Washington, D. C.

Received April 28, 1920

In a study of the freezing points of fruits and vegetables, in which the potentiometer and the needle type of thermocouple were used, a method of making the thermocouples was developed, which has a number of advantages for this kind of work. Thermocouples made by this method are of small size, well insulated, durable, and have a very little lag. The couples are made from silk insulated copper and constantin wire, either 36 or 40 B. and S. gage, as follows:

As many lengths of each kind of wire as there are to be junctions are cut, usually about a meter long, gathered together, and each end of the bundle slipped through a small, hard glass tube. The ends of the wire are dipped in bakelite to cement the insulation solidly, dried, the insulation burned away for about one centimeter, the ends scraped bright and twisted together in pairs, a copper and constantin wire to each pair, for about 3 mm. of the length, and soldered (Fig. 1, A and D). Each junction is then insulated with glass by placing a very small soda glass tube over it and carefully heating in a small flame, the silk covering above the junction being protected meanwhile. At a cherry-red heat the glass softens and shapes itself to the junction, leaving it permanently and completely insulated (Fig. 1, D). The other end of the couple is made in the same way. The selection of the wires in proper sequence is insured by means of a buzzer or by staining the wires different colors before they are bound together.

When the junctions are finished a tube of copper foil about 5 mm. in length is drawn over the bundle above the junctions so that one end extends within the glass tube (Fig. 1, B and C), and cemented in place with bakelite, the exposed portion being wrapped with silk thread. A small brass tube (Fig. 1, C) is usually placed over the junctions also and filled with Wood's metal (Fig. 1, E). With very short junctions, however, this tube is omitted, the junctions being covered with Wood's metal which is dressed down to a thin shell-like tip (Fig. 1, M and N). This type is for use with small objects, such as berries, where the depth of immersion is necessarily limited. It has the disadvantage of a small surface contact and must be made of very fine wire. Even then a high degree of accuracy may not be attained, but it has the advantage of less lag than the first type. One tested had a lag of 0.21 sec., as compared with 0.76 sec. for one of the first type.

In the type first described No. 36 or even larger wire may be used by increasing the dimensions of the other parts proportionally, but it must be remembered that if the diameter of the wire is increased the amount of heat carried away by conduction is also increased as the square. To compensate for this a greater depth of immersion and a greater surface contact at the junctions are necessary.

Any number of junctions from one to fifty or even more can be made, depending on the e. m. f. desired. The number is limited only by the range of the potentiometer and the sensitivity of the galvanometer. A fifty-junction thermocouple of No. 40 wire would be only 2.5 mm. in diameter. The one shown in Fig. 1, E, is a double five, *i. e.*, ten junctions or two groups of five at each end, of No. 36 wire, and is 1.5 mm. in diameter. It has a value of 0.002169° C. per microvolt over a range from 0° to —2° with a lag of 0.76 sec.

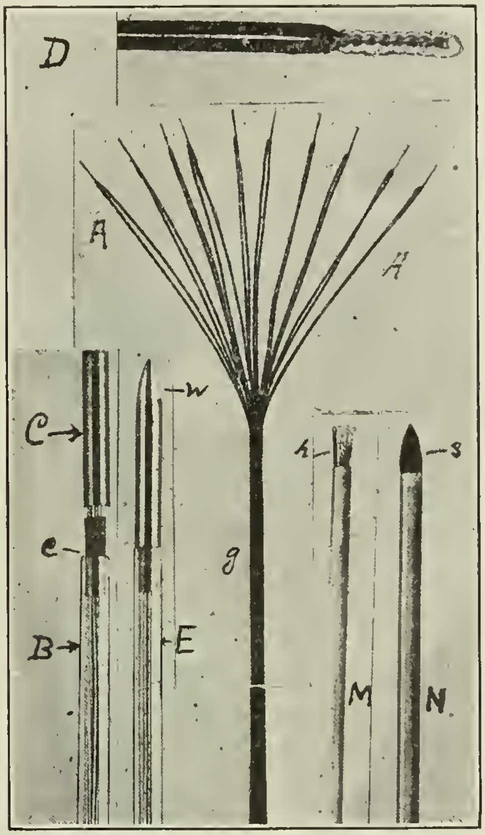

Fig. 1

A—Glass covered junctions of No. 40 wire. *g*—Glass tube through which wires are drawn. D—Single glass covered junction magnified. B—Metal tube C over the junctions. *c*—Small copper tube for strengthening the joint M and N—Type used for berries. *r*—Glass covered junctions. *s*—Same covered with Wood's metal

It is best to have an even number of junctions and sets of leads, each set communicating with half the entire number, as, for example, two junctions with one pair of leads to each group of five. By this means groups can be connected in series and give the full value, or used separately to give half value or connected in opposition to give zero. The last step is to cut one of the copper wires in each group for the leads.

The types described in this paper have a temperature range not higher than 70° C. There is no apparent reason, however, why the range could not be increased by using another one of the alloys, such as Newton's metal instead of Wood's metal or one of the amalgams, such as copper, but for precision work it would be necessary to calibrate for differences greater than a few degrees.

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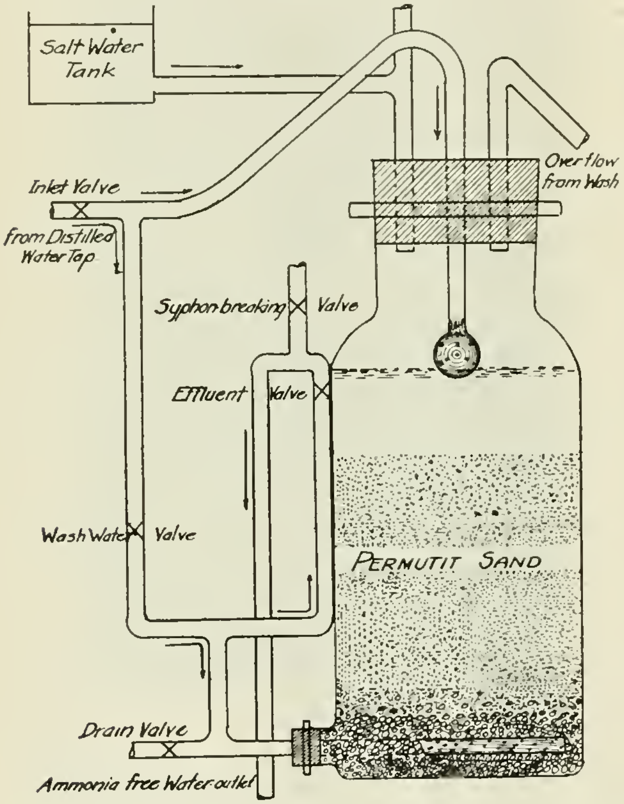
[1] The writer's thanks are due Dr. W. P. White, of the Geophysical Laboratory of the Carnegie Institution, Washington, D. C., and Dr. R. B. Harvey, of the Bureau of Plant Industry, Washington, D. C., for helpful suggestions and assistance in the work described in this paper.

PREPARATION OF AMMONIA-FREE WATER[1]

By Gerald C. Baker

State Water Survey Division, University of Illinois, Urbana, Illinois

In the laboratories of the Illinois State Water Survey Division, large quantities of ammonia-free water are required for nitrogen determination. Until recently the bromine water and sodium hydroxide method has been used in freeing distilled water from ammonia. The distillation was made in a copper still and the process required much time and attention, and was quite expensive. Since January 1, 1918, ammonia-free water has been prepared by passing distilled water through permutit.



Apparatus for Preparation of Ammonia-Free Water

In 1917 Folin and Bell[2] found that when urine and permutit were shaken together the ammonia was quantitatively absorbed, and that it could be again quantitatively liberated by treatment with sodium hydroxide.

It was thought that permutit might be employed in the preparation of ammonia-free water on a larger scale, and an apparatus embodying the principles of the permutit water-softening installation was fitted up. A glass aspirator bottle 30 in. high and 8 in. in diameter was used as a container for the permutit. A layer of glass beads, 1.5 in. deep, was placed in the bottom, and 12 to 14 in. of permutit were placed on top of the beads. During operation the distilled water enters the top of the bottle through a tube connected to a faucet. For back flushing, a tube to carry distilled water, equipped with a valve, enters the bottom of the bottle. This tube serves also as a bottom drain through which the ammonia-free water passes to a tube rising almost to the height of the water in the bottle and containing an opening in the top to prevent siphoning effects. An overflow pipe is provided for use during the back flushing of the filter. A 2-gal. glass bottle having an opening at the bottom elevated above the filter is used for containing the salt solution and feeding it to the filter while regenerating. The distilled water is distributed over the surface of the permutit by a perforated glass bulb. The water is allowed to flow slowly through the permutit at the rate of about one gallon per hour. With 3 gal. of permutit it has been possible to prepare, before regenerating, 100 gal. of ammonia-free water, having started with a distilled water containing 0.7 part per million of ammonia.

Regeneration is accomplished by passing 2 gal. of a 10 per cent common salt solution on to the filter, and letting it stand over night, then washing the filter in a manner similar to the washing of any permutit machine.

It is a question whether the removal of ammonia by this reagent is strictly a displacement phenomenon, or whether the displacement is accompanied by some mechanical absorption of the ammonia. The permutit itself is, of course, a complex hydrated sodium aluminum silicate containing easily replaceable sodium. If we represent such a typical hydrated silicate, chabasite, which has the formula $Na_2Al_2Si_4O_{12}.6H_2O$, by its empirical graphical formula[1] $(OH)_3Si\text{-}O\text{-}Si(OH)_2OAl(OH)(ONa)$, we get an idea of the ease of replaceability of the sodium. In practice much of the replaceable sodium remains when the machine begins to deliver a water containing ammonia, for it will still remove large quantities of hardening constituents before recharging.

It is quite evident that there is a mass relationship between the ammonia absorbed and the ammonia present in the water, and when a certain amount of sodium is replaced an equilibrium is established when the removal of ammonia is not quantitative.

It was not possible to make ammonia-free water from the University of Illinois supply, a relatively hard water, even though the water was passed through the permutit at as slow a rate as possible. This would indicate that there is also a mass relationship between the removal of the ammonia and the salts present in the water.

An analysis of a representative sample of the distilled water used in the preparation of ammonia-free water showed a mineral content of 17 parts per million, largely sodium carbonate.

The permutit used in the preparation of ammonia-free water has not deteriorated appreciably with use, and is as active as when first put in use 2 yrs. ago. It is, however, appreciably soluble and at times deposits are formed on the walls of the storage vessels. It is necessary to remove these deposits at intervals of 2 to 3 mo., as they contain an appreciable amount of ammonium salts.

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[1] Read at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

[2] *J. Biol. Chem.*, **29** (1917), 329.

[1] *Proc 8th Intern. Cong. Appl. Chem.*, **25**, 125.

SUMMARY

This permutit method of preparing ammonia-free water is applicable if distilled water is used. It has advantages over other methods of preparation in ease of operation and production of large quantities at minimum expense. The disadvantages of the method are that it gives a water of higher mineral content and does not remove nitrate, nitrite, or albuminoid nitrogen.

Investigations made thus far would indicate that the American permutit, except the prepared Folin permutit, will not quantitatively remove ammonia. German permutit has proved very satisfactory, and indications are that the English permutit is equally efficient. There is a possibility that Refinite and Boromite may possess similar properties.

ACKNOWLEDGMENT

The author wishes to express his appreciation to Prof. Edward Bartow, chief of the Illinois State Water Survey Division, and to Mr. R. E. Greenfield for their assistance and criticism during the preparation of this paper.

NOTES ON THE PREPARATION OF CUPFERRON

By D. R. Kasanof

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Received April 15, 1920

In view of the increasing importance of cupferron as an analytic reagent, it is believed that a slight modification of the method of preparation of Baudisch and King[1] may be of assistance in securing a consistently good yield. The method commonly employed has its weakest link in the preparation of the phenylhydroxylamine, the yield of which varies from zero to 70 per cent of the theory, depending on the quality of the zinc dust employed. Poor yields are probably due to a microscopic coating of zinc oxide on the surface of the zinc dust. The author has obtained a consistently good yield of phenylhydroxylamine from nitrobenzene by using amalgamated zinc dust.

Sixty grams of nitrobenzene are thoroughly emulsified by vigorous stirring in 700 cc. of water, containing 30 g. of ammonium chloride, in a wide-mouthed jar or a beaker of 1.5 to 2 liters capacity. Eighty grams of zinc dust are amalgamated with a 2 per cent solution of mercurous nitrate, acidified with a few cc. of nitric acid. After stirring this mixture for a few minutes the zinc dust is permitted to settle and the supernatant liquid is poured off. The zinc dust is washed with water, under suction, until free from acid, and may then be introduced without drying, a small portion at a time, to the nitrobenzene emulsion. Vigorous stirring throughout is essential. The temperature tends to rise after each introduction of the zinc dust paste and must be kept at about 16° C. by the introduction of chipped ice. All the zinc dust should have been added within one hour, and the volume of liquid in the jar will have increased to a liter, or more, from the ice introduced. After complete reduction, the zinc hydroxide is filtered off with suction, the filtrate cooled to 0° C., and sodium chloride in an amount calculated to saturate the volume of filtrate is added. A voluminous precipitate of phenylhydroxylamine is soon thrown down, which, after standing 15 min., is filtered off with suction and pressed well between filter paper. (Caution: Phenylhydroxylamine is a violent skin poison. Rubber gloves should be worn and care taken of the face and eyes. Alcohol is the best remedial application.)

The slightly damp phenylhydroxylamine is dissolved in 500 cc. of ether and allowed to stand over night in a closed flask in contact with fused calcium chloride. The ethereal solution is filtered through filter paper, cooled to 0° C., and saturated with dry ammonia gas, prepared by gently warming strong ammonium hydroxide and drying the gas evolved by passing through one or more drying bottles packed with broken sticks of sodium hydroxide. To the resulting ethereal solution of the ammonium salt, 60 g. of cold, freshly distilled amyl nitrite are now added all at once. The vessel becomes filled with crystals of cupferron and the temperature rises considerably, some ether possibly boiling off (Hood). The precipitate is filtered at the pump, washed with a little ether, and spread on filter paper in a cool place to dry. The cupferron thus obtained is best preserved in a wide-mouthed, glass-stoppered bottle, in which a lump of ammonium carbonate is placed. This may be wrapped in filter paper and suspended by a cotton thread attached with sealing wax to the stopper.

Amalgamated zinc dust may be used to equal advantage in other similar reactions.

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[1] This Journal, **3** (1911), 629.

NOTE ON THE USE OF ALUNDUM FILTERING CRUCIBLES

By D. T. Englis

Department of Chemistry, University of Illinois, Urbana, Illinois

Received April 28, 1920

One of the many uses of porous alundum ware is in filtering off cuprous oxide in the determination of reducing sugars. In a study made by Meade and Harris[1] on the determination of these sugars in cane products, a very close agreement is reported between comparative tests with Gooch and alundum crucibles.

In similar experiments made by the writer difficulty was experienced in securing complete washing. Even though the Sargent crucible holder was used there was a tendency for the soluble alkali and copper salts to climb to the upper edge of the porous crucible and escape removal. Spencer's[2] filtering apparatus would doubtless have eliminated this difficulty, but since one of these was not at hand it was necessary to resort to some other method.

The procedure finally adopted was to insert the crucible in the Sargent holder, but with the flange downward, as shown in the accompanying figure. Washing was then carried out as completely as possible in the usual way. When all the soluble material had been removed, except the small amount in the upper rim, the crucible was filled about half full of water, suction was applied and a moistened rubber stopper was quickly pressed down on top of the crucible. (The rubber stopper was always polished to a plane surface and washed free from any dust before using the first time.) As soon as the stopper was firmly held by the suction, water was poured on top of the holder (see figure) and around the stopper. The water drawn through the top rim easily completed the washing, as was indicated by the fact that no test for alkalinity could be obtained by addition of a drop of phenolphthalein to the edge of the crucible.

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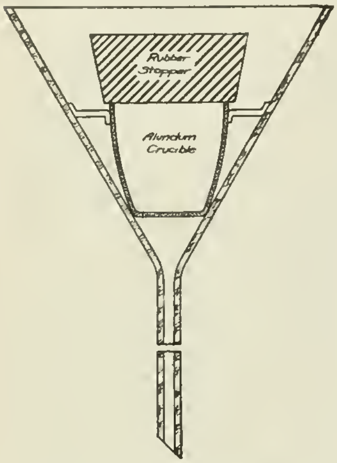
[1] This Journal, **8** (1916), 506.

[2] *Ibid.*, **4** (1912), 614.



Continuous use of the crucible holder, since it was not designed for treatment in this manner, tended to crack the flange from the outer portion of the holder. A slight modification of the flange construction would perhaps lessen this difficulty.

RAPID DETERMINATION OF SMALL AMOUNTS OF COPPER BY THE IODIDE METHOD

By H. F. Bradley
Park City, Utah

Received April 5, 1920

The precipitate of cupric sulfide (containing not over 0.05 g. copper) is washed free from chlorides (complete removal of iron not being necessary), then moistened with a few drops of strong neutral zinc nitrate solution (free from chlorides), and ignited.

The residue of zinc oxide and cupric oxide is quickly dissolved by warming with 1 cc. of 1 : 2 hydrochloric acid. Neutralize with 5 per cent potassium hydroxide, acidify with acetic acid, add a little phosphate solution to prevent the action of iron,[1] then add 2.5 g. solid sodium iodide and titrate as usual.

SOME AMERICAN-MADE CHEMICAL REAGENTS

By W. D. Collins
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Washington, D. C.

Received March 31, 1920

I—POTASSIUM FERRICYANIDE

A member of the American Chemical Society informed the Committee on Guaranteed Reagents that he had found potassium ferricyanide purchased a year or two ago wholly unsuited for use in making the gelatin test on tin plate. The salt made a turbid green solution.

Examination of two lots which had been in the Bureau of Chemistry for several years showed that they were of the same quality, but a single recrystallization from a filtered solution gave a perfectly satisfactory product.

Correspondence with manufacturers and dealers secured some analytical reports which indicated material of high purity. A sample furnished as representing the product now sold by one manufacturer made a perfectly clear 10 per cent solution with no traces of green color and no precipitate.

It therefore appears that no one need now accept potassium ferricyanide which will not make a 10 per cent solution without any precipitate or green color. Purification of poor material in stock is worth while in most cases.

II—METHYL ORANGE[1]

Similar complaint was made to the Committee of difficulty in procuring satisfactory methyl orange from American manufacturers. At the suggestion of the Committee, samples were purchased from four different sources. There was at hand for comparison one of a well-known foreign make. A sixth sample was obtained from a lot of methyl orange which was exhibited by a manufacturer at a meeting.

A few grams of the best appearing sample (Sample A) were repurified by precipitating the free acid, filtering, dissolving with sodium carbonate solution, and recrystallizing twice. This produced shining crystal leaflets of a beautiful orange-red color which were provisionally adopted as a standard.

The samples were judged by general appearance, odor, water-insoluble residue from one gram in 400 cc. of water, and indicator value. The results are given in the accompanying table.

COMPARISON OF SAMPLES OF METHYL ORANGE

SAMPLE	Appearance	Odor	Water-insol. Residue from 1 g.	Indicator Value	Notes
Standard	Orange-red crystals	None	0.0000	Good	
A	Orange-red crystals	Very faint	0.0008	Good	
B	Yellow-red powder	None	0.0294	Good	Foreign-made
C	Yellow-brown, lumpy[1]	Decided	0.0105	Good	
D	Brown, lumpy	Decided	0.0537	Fair	Dyestuff
E	Brown powder	Strong	0.1167	Good	Naphthol-like odor
F	Yellow-red powder	None	Slight	Good	

[1] A later sample from the manufacturer of C compared favorably with B or F.

The odor resembled aniline in three cases, and one sample smelled strongly like naphthol.

The two brown samples were not very pleasing in appearance. The manufacturer of one of these products stated in reply to criticism of his output that it was not intended for an indicator but was sold for use as a dyestuff.

A portion of Sample D was purified both by direct recrystallization and by precipitating the acid and subsequently neutralizing the free acid with soda. In each case a bronze-yellow crystalline powder was recovered which, in appearance, did not resemble the standard methyl orange. When used as an indicator its alkaline solution was bright yellow in color, but the acid solution was only pale red. Sample D did not give a clear solution when filtered.

Notwithstanding the poor quality of some of the samples obtained, the results show that it is entirely possible at this time to secure a very satisfactory grade of methyl orange. It is recommended that purchasers specify methyl orange of a grade to be used as an indicator and also stipulate that the insoluble residue from one gram dissolved in 400 cc. of water shall not exceed 0.025 g.

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[1] R. H. Deakin, *Chem. News*, **118**, 193.

[1] In collaboration with G. C. Spencer.

III—SULFURIC ACID FREE FROM NITRATE: THE DIPHENYLAMINE TEST FOR NITRATES[1]

The diphenylamine test for nitrate has been studied carefully by J. Tillmans,[2] who reviews previous work and describes the best conditions for making the test. The most satisfactory reagent is prepared by dissolving 0.017 g. of diphenylamine in 100 cc. of concentrated sulfuric acid (sp. gr. 1.84), and adding 30 cc. of water.

At a time when there was no sulfuric acid in the Bureau of Chemistry which would give a colorless reagent, four producers and dealers were asked whether they could furnish such acid. Dealer A stated that they had never handled acid which would give absolutely no color under the conditions described, but that one grade furnished by Maker C was the nearest this quality which they had received. Producer B stated that they could not furnish acid which would not give a trace of green color, but at a later date stated that they were then able to furnish the required acid on request. Producer C stated that they could furnish such acid if reference was made to their letter on the subject. This acid proved perfectly satisfactory for making the reagent. Producer D stated that all their acid was of the quality desired. One bottle was ordered for examination. The blue color developed on making the reagent was darker than was obtained with any of the samples of acid on hand in the Bureau, and the acid was returned to the dealer.

This experience shows that sulfuric acid can be secured which will serve for preparing the diphenylamine reagent, but this grade must be specified clearly, and purchased subject to examination.

The very low limits for sensitiveness reached by Tillmans were not found in the tests for nitrates in sulfuric acid. He and others have pointed out the number of other substances which produce the blue color. It must be understood that a positive test does not prove the presence of nitrates, but a negative result shows the absence of the minimum quantity necessary to give a test.

METHOD OF NITRATE TEST

A number of methods of applying the diphenylamine test were tried in order to select one which would serve to assure sulfuric acid sufficiently free from nitrates for careful analytical work without making the test too exacting. The U. S. Pharmacopeia test prescribes mixing the acid with nine volumes of water and pouring the mixture carefully over a reagent made with 0.5 g. of diphenylamine dissolved in 100 cc. of sulfuric acid and 20 cc. of water. Sulfuric acid containing 0.02 per cent N_2O_5 gives a blue ring at the place of contact of the two layers. Acid with 0.01 per cent N_2O_5 gives no color.

A simple application of the test is to add a drop or two of the U. S. Pharmacopeia reagent to 3 to 5 cc. of the acid in a test tube and overlay with water. A blue ring develops in 10 min. if the acid contains 0.00002 per cent of N_2O_5. With 0.00001 per cent the ring is seen in some instances and not in others.

When 2 cc. of sulfuric acid are mixed with 1 cc. of water and there are added immediately to the mixture 1 cc. of reagent made with 0.017 g. diphenylamine, 100 cc. of sulfuric acid (sp. gr. 1.84), and 30 cc. of water, a decided blue color develops in 10 min. if the acid contains 0.00005 per cent N_2O_5. If the mixture of acid and water is cooled to 20° C. before addition of the reagent, no blue color is developed in 10 min. if the acid contains less than 0.0001 per cent N_2O_5. Nearly all the reagent sulfuric acid on the market will pass this test.

The presence of too large a quantity of diphenylamine interferes with the test. Increasing the proportion of either water or sulfuric acid in the reagent as described by Tillmans makes the test less sensitive. The preparation of the reagent is thus the most delicate test for the presence of nitrates, nitrites, or some of the other substances which give the blue color with diphenylamine. Sulfuric acid containing 0.000008 per cent N_2O_5 shows a decided faint blue color in 2 hrs. after preparing the reagent. Acid with less nitric present will serve to prepare a reagent which will be perfectly colorless.

Acid of this grade can be purchased if it is specified that this test must be met.

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[1] In collaboration with James K. Morton.

[2] *Z. Nahr. Genussm.*, **20** (1910), 676.

ADDRESSES AND CONTRIBUTED ARTICLES

CERTAIN ASPECTS OF THE CHEMISTRY OF CELLULOSE ACETATE FROM THE COLLOIDAL VIEWPOINT[1]

By Gustavus J. Esselen, Jr.
Arthur D. Little, Inc., Cambridge, Mass.

If one were asked for a good example of a colloidal solution in a non-aqueous solvent, probably among the first materials to come to mind would be solutions of cellulose esters. In spite of this, it is only comparatively recently that the colloidal character of the parent substance cellulose has been recognized. Harrison[1] has correlated in a most interesting manner many of the reactions of cellulose, as, for example, its behavior when treated with alkalies, acids or oxidizing agents, by considering the typical cellulose, cotton, as existing in a number of different degrees of colloidal dispersion. Cross[2] has also referred to cellulose as a colloid, and Miss Minor[3] has recently considered the hydration of cellulose in paper making from the standpoint of colloid chemistry. Whether or not the solution of the problem of the constitution of the cellulose molecule is ultimately to be found in these colloidal considerations, the point of view which they present is certainly helpful in correlating many previously unconnected observations. Once it is admitted that cellulose is a colloid, all its transformations are to be considered as colloid chemical processes and as such involve one or more of the various phenomena, such as adsorption, change in degree of dispersion, etc., which we have come to associate with materials in the colloidal state.

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[1] Read at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

[1] *Trans. Nat. Assoc. Cotton Mfgrs.*, **101** (1916), 201. 2nd Report on Colloid Chem., Brit. Assn. Adv. Sci., **1918**, 52.

[2] *J. Soc. Dyers Colourists*, **34** (1918), 92.

[3] *Paper*, **25** (1919), 700.

This is not the place, nor is there time, to discuss at any length the underlying principles of colloid chemistry. There is, however, one phase of the matter which it is well to keep constantly in mind, and that is, that in substances dispersed colloidally the surface is unusually great in proportion to the mass. This being so, we should expect all surface phenomena to be emphasized. We shall have special occasion to refer to the particular surface phenomenon of adsorption, which Langmuir[1] considers to be intimately connected with the time lag between the striking of an ion or molecule on a surface and the rebounding from that surface. This gives a picture of the process which helps to fix in the mind some of the particular steps which are referred to later. Miss Minor[2] has pointed out that where cellulose is under consideration, another of Langmuir's postulates also seems to have particular significance: that is, his definition of a colloid molecule as a large aggregate of atoms or group molecules held together by secondary valence.

CATALYTIC ACTION OF SULFURIC ACID

In its simplest terms, cellulose acetate is formed by the esterification of cellulose by means of acetic anhydride in the presence of a catalyst. There are two general methods of producing cellulose acetate, both of which have a number of variations. One results in a fibrous acetate resembling in outward appearance the original cotton used as raw material; the other gives a granular product. In all methods the most common catalyst is sulfuric acid dissolved in acetic acid, which acts as a carrier. In some instances the cellulose is first given a preliminary treatment with the mixture of sulfuric and acetic acids, sometimes in the presence of a little water. The treatment is often referred to as a hydration, but its exact nature has not been established. Whether or not a preliminary treatment is given before adding the acetic anhydride, the sulfuric acid is adsorbed by the cellulose from the solution. These sulfuric acid-cellulose compounds were at one time considered to be true molecular compounds, but they are now recognized as adsorption compounds, forming a series in which the percentage of sulfuric acid varies by much more gradual changes than could be accounted for on the basis of simple molecular proportions. This either results in, or is accompanied by a swelling and peptization of the cellulose to an extent depending upon the temperature and time. As indications that the degree of dispersion is really modified, there may be cited the observations that the longer the preliminary treatment, the more rapid the subsequent esterification and the less viscous the solutions of the product. The success of the process is doubtless due quite as much to the modification of the colloidal state of the cellulose as to the usual effect of the catalyst in facilitating esterification. In this latter connection it may be noted that because of being right on the surface where the reaction must take place, the catalyst is in a peculiarly effective situation for promoting the esterification.

In making the granular form of cellulose acetate, cellulose, usually in the form of cotton, is treated with a mixture of acetic acid, acetic anhydride, and a suitable catalyst. The acetic acid acts merely as a carrier and takes no part in the reaction. As mentioned above, the catalyst dissolved in acetic acid is frequently mixed with the cellulose some time before the anhydride is added, although in other cases all are added together. Since cellulose acetate is soluble in acetic acid, the cellulose dissolves as the esterification proceeds. Samples are taken from time to time and when the desired solubility has been attained, the reaction is stopped by adding an excess of water which destroys any remaining anhydride and precipitates the cellulose acetate. In the earlier processes, the acetate thus formed was the tri-acetate corresponding to the hexanitrate. It later developed[1] that owing to their wider range of solubility the acetates of most technical usefulness were those with a somewhat lower acetyl content than would correspond to a hexa-acetate on the C_{12} basis, but higher than would correspond to a penta-acetate. These were at first prepared by adding small and carefully regulated amounts of water and sulfuric acid to the solution of cellulose acetate in acetic acid. As before, when the desired solubility was attained, the product was isolated by precipitation with water. While outwardly this secondary treatment is one of partial saponification, it is actually much more intimately connected with the colloid properties of the cellulose acetate. The reason for this statement is that an equivalent degree of saponification obtained by methods not involving the solution of the acetate does not give a product with the same wide range of solubilities. The effect may very possibly be connected with the opening up of the molecule in such a way as to make the —CO group more reactive, because it results in a greatly increased solubility in acetone.

In preparing cellulose acetate in fibrous form, it is given a preliminary treatment with sulfuric acid dissolved in glacial acetic acid, this step being similar to the one for preparing granular cellulose acetate. After removing the surplus preliminary bath in a centrifuge or press, the cellulose is immersed in a mixture of acetic acid, acetic anhydride, and some nonsolvent hydrocarbon like kerosene, or benzene. While the proportion of non-solvent is so regulated that the cellulose acetate does not dissolve, the conversion is accompanied by a marked swelling and by a noticeable change in the index of refraction. When the product has reached the desired degree of solubility, the surplus bath is removed, and the residue thoroughly washed with water. The product is cellulose tri-acetate, which is subjected to a partial saponification to render it soluble in acetone.

CELLULOSE ACETATE SOLVENTS

One of the earliest solvents for cellulose acetate was chloroform, and it was soon noticed that solutions in this solvent were markedly improved by the addition of small amounts of alcohol. The improvement in solubility passes through a maximum and then gradually falls off until finally a proportion of alcohol is reached which gives a mixture with chloroform in which cellulose acetate is no longer soluble. So far as I know, no explanation has ever been offered for this behavior. A possible explanation may be found if we remember that cellulose and its compounds have marked affinity for hydroxyl groups. In fact, if the size of the negative charge[2] assumed when immersed in water is a reliable criterion, cellulose acetate has a considerably greater affinity for hydroxyl groups than cellulose has. When alcohol is added to a chloroform solution, it may be that the cellulose acetate adsorbs the alcohol, in which case the hydroxyl groups would probably be next the cellulose acetate, and the hydrocarbon radicals would be sticking out into the solution. Reasoning from the analogous effect of a dilute sodium hydroxide solution on cellulose, a slight swelling of the cellulose acetate might well be assumed with the possibility of an accompanying increase in dispersion. This may be one of the effects entering into the improvement in solubility when alcohol is added. A second effect may be that the hydrocarbon groups exert more of an attraction on the hydrocarbon end of the chloroform molecule than does cellulose acetate itself, which would also tend to improve the solubility. The maximum point in the curve may correspond to the point at which all the secondary valences of the surface of the cellulose acetate are just saturated with alcohol. Since the cellulose acetate is in a colloidal degree of dispersion, its surface will be large and a considerable amount of alcohol will be required. In practice, this point is reached when alcohol constitutes about 25 to 30 per cent of the solvent mixture. Inasmuch as alcohol is not itself a solvent for the usual forms of cellulose acetate, any more than dilute caustic soda solutions are solvents for cellulose, it is natural that further additions of alcohol should gradually tend toward making the mixture a non-solvent. There is a further analogy between the action of dilute caustic soda solution on cellulose and that of alcohol on cellulose acetate, in that certain forms of cellulose acetate are known which are soluble in hot alcohol, corresponding to those forms of cellulose precipitated from zinc chloride or cuprammonium solutions, which are soluble in aqueous alkalies.

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[1] *J. Am. Chem. Soc.*, **36** (1914), 2221; **39** (1917), 1849.

[2] *Loc. cit.*

[1] Ost, *Z. angew. Chem.*, **32** (1919), 66, 76, 82; *Chem. Abs.*, **13** (1919), 2760.

[2] *Trans. Nat. Assoc. Cotton Mfgrs.*, **101** (1916), 218.

Another interesting example of the beneficial effect of alcohol is in connection with aromatic hydrocarbons. Cellulose acetate is not soluble in benzene either at room temperature or at the boiling temperature. However, if a certain amount of alcohol is added to the benzene, the mixture becomes a solvent for the cellulose acetate when warmed. This is true even with those varieties of cellulose acetate which are not soluble in hot alcohol. Here again, we may have the same explanation as in the previous instance, *i. e.*, the alcohol may be adsorbed and the hydrocarbon radicals may be sufficiently attracted by the benzene to cause the cellulose acetate with its adsorbed alcohol to go into solution.

One might, at first sight, think that if this proposed theory were correct, mixtures of aliphatic hydrocarbons and alcohol should also be expected to act as solvents for cellulose acetate, which is not the case. On further consideration it will be seen that the fact that aliphatic hydrocarbons and alcohol are not solvents for cellulose acetate is merely another piece of evidence that the theory is really the true explanation. From the fact that heat is required to effect the solution of cellulose acetate in mixtures of benzene and alcohol, we may conclude that the attraction between the adsorbed alcohol and the benzene is very near the minimum amount required for solution. If the attraction were very much less, we should not get the resulting solubility. Now we know that benzene has much more of an attraction for alcohol than have the aliphatic hydrocarbons ordinarily met with in petroleum solvents such as gasoline or kerosene. These relative attractions are well illustrated by the fact that kerosene and gasoline are not miscible with ethyl alcohol, except in very small proportions, whereas alcohol and benzene are readily miscible. Therefore, since the attraction between benzene and alcohol is just about the minimum necessary to bring the cellulose acetate into solution, and since the attraction between alcohol and the ordinary aliphatic hydrocarbons is distinctly less, it is not to be expected, if the proposed theory is correct, that the latter mixtures would be solvents of cellulose acetate. It is seen, therefore, that the solubility in alcohol and chloroform is intimately connected with the solubility in alcohol and benzene.

As an outcome of this consideration of the reason for the solubility of cellulose acetate in mixtures of benzene and alcohol, it would naturally be expected that if the theory held true, such materials as combined an aromatic radical and a hydroxyl group in one molecule should also be solvents for cellulose acetate. This is known to be true, since the phenols as a class are among the very best solvents for cellulose acetate.

To sum up, it is pointed out that it is not unreasonable to expect that when ethyl or methyl alcohol is added to a chloroform solution of cellulose acetate, the alcohol is adsorbed by the colloidal cellulose acetate, the hydroxyl groups probably being nearest the surface of the cellulose acetate particles. The resulting improvement in solubility which occurs may then be explained as due to a combination of two effects: first, a swelling and possible increase in the degree of dispersion of the cellulose acetate; and second, a greater attraction for the chloroform by the simple hydrocarbon radical of the alcohol than by the more complex cellulose acetate. The theory is extended to explain the solubility of cellulose acetate in mixtures of alcohol and benzene and in phenols, which, as a class, are excellent solvents for cellulose acetate.

There are, then, two classes of solvents for cellulose acetate whose solvent properties may be, to a certain extent, at least, explained. In the first class are those solvents like acetic acid, ethyl acetate, and triacetin which contain acetyl groups and whose solvent action is to be explained on the ground that they are presumably of the same general type as cellulose acetate. In the second class are certain compounds and mixtures containing hydroxyl groups combined with aromatic or certain of the simpler aliphatic hydrocarbon radicals, the solvent action of which has been explained above.

It is recognized that there are still other solvents of cellulose acetate which are not included in either of the above general divisions, and it is hoped that a correlation can later be made of many of the observed phenomena in these instances also.

CHEMICAL CONTROL IN THE BEET SUGAR INDUSTRY[1]

By S. J. Osborn

THE GREAT WESTERN SUGAR COMPANY, DENVER, COLORADO

The chemical control of a beet sugar factory may range from almost nothing up to the work performed by a large and highly complex organization. It is the purpose of this paper to give some idea of the activities of a chemical department of the latter type.

The beet sugar chemist was formerly a poorly paid individual who was expected to do a certain amount of laboratory work with the help of perhaps one or two assistants. He was frequently a man of very limited technical education, and, owing to the fact that a beet sugar factory operates for only three or four months during the year, the chemist was often considered of not sufficient importance to be kept on the payroll after the end of the campaign, or operating season. Naturally this did not conduce to the development of a high grade of work or to the standing of the chemist in the industry.

In some companies of sufficient size the chemical control work is now handled by a specially organized chemical department, entirely independent of the operating department, although the two naturally enjoy intimate relations and must work in close coöperation to achieve the best results. This system has many advantages. Not only does it relieve the operating department of responsibility for a highly technical line of work, but it puts the results on a basis where they are free from even any suspicion of bias or irregularity, and facilitates the introduction and use of uniform methods of analysis and control at all factories of the organization. Naturally it does not pay to develop an elaborate system of chemical control unless the operating and engineering departments are also sufficiently developed to use and apply the data, and the growth of the several departments will therefore go hand in hand.

METHODS OF CHEMICAL CONTROL

While the beet sugar manufacturing process is not a highly complicated one, as chemical processes go, it is doubtful if any other manufacturing process is so closely and thoroughly controlled at every step by the chemical laboratory.

An important factor in the development and application of chemical control in all branches of the sugar industry is the

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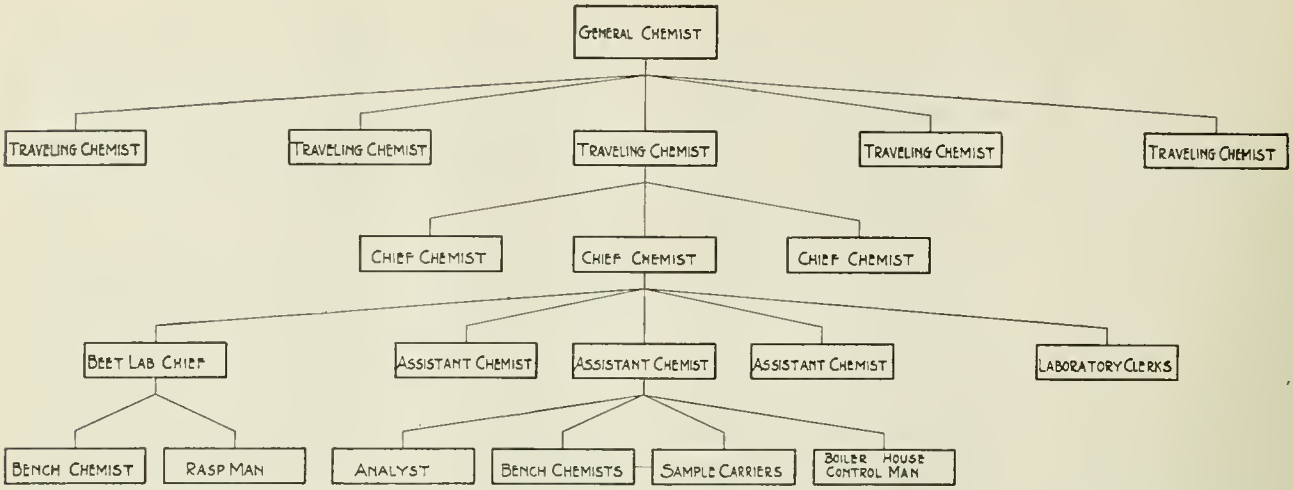
[1] Read at the 59th Meeting before the Sugar Section of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.



Organization Chart

extent to which rapid and reliable control methods have been worked out. The polariscope, which has supplanted the older, time-consuming, chemical methods for the determination of sugar, is the principal and indispensable tool of the sugar chemist, and it is not too much to say that without it the sugar industry would still be in the dark ages.

The Brix hydrometer and the refractometer have similarly proved of great value for the estimation of the apparent dry substance, which, together with the polarization, establishes the "apparent purity," a figure which is a *sine qua non* in the operation of a sugar factory. Many other methods could be described, if time permitted.

To avoid the impression that the laboratory work may be of a wholly superficial character, it should be stated that the rapid methods are used to handle a large volume of work and yield immediate information, but enough work is done by the most reliable methods known to furnish all the fundamental information which is believed to be of value.

SCOPE OF A CHEMICAL DEPARTMENT

In our organization the Chemical Department has a wider field than its name might strictly indicate. It issues and is responsible for almost all of the important operating reports, other than financial, and keeps a detailed set of records for this purpose. It secures all the necessary data for the calculation of extraction losses. The chemist is therefore responsible for testing the automatic beet scales, for weighing the molasses, and for obtaining accurate records in general throughout the factory. Naturally the laboratory is called on for information and advice in solving the numerous technical problems which arise, and its assistance can be of the greatest value.

The Chemical Department also accumulates a great mass of data which is of the nature of general information and may not be of immediate application, but nevertheless has a great potential value. In the first place, it furnishes a record of many campaigns' experience by which new technical questions may in many cases be answered and future policies may be decided, and, in addition, it has been our experience that from such data general laws have been deduced which have been of the utmost importance in their application to prevailing conditions. One of the problems of the Chemical Department is the question of the extent to which work that does not have an immediate application shall be carried out.

WORK OF A CHEMICAL DEPARTMENT

Some figures on the amount of work done in the laboratory of one of our beet sugar factories may be of interest. The amount of work is dependent not so much on the size of the factory as on whether or not it is equipped with the Steffen process, or with a pulp dryer, or with both. The following statement shows the approximate number of the common tests made per 24 hrs. in one of our average laboratories.

200–300	Polarizations
150–200	Apparent purity determinations
125	Brix determinations (reported)
175–225	Alkalinity determinations on juices
60	Determinations of CaO by titration on lime cake, lime, etc.
30–60	Determinations of CaO by soap solution
225	α-Naphthol tests on condensed waters
200	Temperature readings in the factory

Each factory also maintains a special beet laboratory, the work of which has consisted of from 100 to 500 polarizations per day of beet samples of 25 lbs. each. If the beet growers are paid on a sliding scale based on sugar percentage, as was formerly the case, the beet laboratory tests determine the basis of payment to the farmer. Otherwise the tests are made as a matter of information for the Agricultural Department, as it is important that it should have accurate data on the quality of the beets, not only as a whole, but also in different districts and at different periods of growth.

PERSONNEL

The personnel of the laboratory organization at a single one of our factories varies in number from 22 up to 42, who, with a few exceptions, work in 8-hr. shifts. The accompanying organization chart will explain how the work is handled.

The General Chemist is the head of the department. Directly under him are five Traveling Chemists, each of whom has supervision over the work of the department at three or four contiguous factories and has his headquarters at one of the factories with which he is connected. The Chief Chemist, who in turn is responsible to the Traveling Chemist, is the head of the local factory organization and has no routine duties. There are three Assistant Chemists at every factory, one on each shift. The Assistant Chemist has charge of the laboratory employees on his shift, and in addition has a certain amount of analytical work, and work in the factory such as the supervision of the sampling, the testing of the beet scales, reading of meters, etc. The Bench Chemists, of whom there are three or four on each shift, perform the routine tests, while the Analyst takes care of the extra analytical work demanding a higher degree of skill. In some cases the Assistant Chemists handle all of this work and there are no special analysts, while in other cases, where the volume of work is greater, one or two analysts are employed. The Boiler House Control Man collects samples of coal and ashes, makes flue-gas analyses, and secures various data in the boiler house from which a complete heat balance is calculated every day.

The Chief Chemist has charge of the laboratory clerical work, for which purpose two to three clerks are employed; this is by no means a small part of his responsibility. He also supervises the work of the beet laboratory, which has been previously described.

Our customary intercampaign laboratory personnel at each factory consists of the Chief Chemist and one or two Assistant Chemists. From this nucleus there must be built up every year for the campaign work an organization of the kind just described. The beet sugar industry has its peculiar problems and this is one of them. It should be remembered that this organization problem is one that has to be met not once in a long period of time, but is a yearly part of the work to which the Chief Chemist has to look forward. To get a new laboratory organization working smoothly in a short period of time is by no means an easy task and demands a high degree of executive ability in addition to the technical knowledge required.

DYE RESEARCH[1]

By Robert E. Rose

Chemical Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware

We are very certain that this country possesses the materials and men to assure the success of the dye industry; we have the raw materials for all that is necessary; our chemists have shown that they can convert these into very excellent finished products; but, granting this, it still remains true that we have a long way to go before our resources are put to the best use. As a whole, our dye industry is rather like a process which is past the semiworks stage but is not yet a smoothly running plant operation. It is for us to do all that we can to realize what is yet needed and to put every effort into making those things, which we see are necessary, a part of the industry.

For my present purpose, I wish to point out that we are as yet digging up treasures fashioned and hidden by others. We have yet to hear that an American house has produced an entirely original and very valuable contribution to the list of commercial dyes. We have yet to read papers embodying the successful results of American academic research which open new fields for the industrial dye chemist.

Is it too early to think of doing all that may be done to speed the time when American names will be mentioned as originators in our chosen field? I do not think so, and I am here to tell you what I think should be attempted in order to insure our future.

Research we must have, not a mere checking up of recipes, not a mere search for information which is known to others, but not to ourselves; that type of work has been exaggerated out of all semblance to its real value simply because of the fact that we have had to start with hardly any knowledge of this particular chemical industry and we have been going through a sort of undergraduate course in dye chemistry. No, that is not what will keep us ahead; we must graduate to real research; that is, enter the entirely unknown and either apply known generalization to new cases; or, and this is the higher faculty, take known facts, add to them, and then generalize in such a way that new ranks of facts stand at our command. Of these two types of research, as I see it, one falls within the province of industrial organizations, the other almost exclusively to academic thinkers, using the word "academic" to denote any investigational activity which is not prompted by immediate utilitarian motives.

If my assumption is correct, it is clear that we, who must make research pay its way, are vitally interested in fostering that research which, though in reality more productive, is not so evidently based on financial returns. No one can tell a research chemist outside of the industry what he should study. The very essence of academic research is absolute freedom, even from the bias which comes from industrialism, and it is almost impossible for an industrial organism to see with unbiased eyes. But, on the other hand, the highest theoretical achievements have always come from a close attention to facts. Let us then furnish the facts and let the academician use them in any way he sees fit. We should then draw his attention to the subject, hardly more than that.

Here we come to the first apparent stumbling block to that very necessary coöperation between those occupied in pure science and those who produce according to the methods of science. This is industrial secrecy, a very dangerous weapon because it is not alone two-edged, but double-pointed. All I can say is, that I hope the day may come when secrecy is no longer a necessity. In the meantime, we must admit that it must be observed. I should like to see it mitigated to this extent, at least, that any real research chemist who is doing important academic work should have access to any and all industrial plants and to the methods followed in those plants, he being on his word of honor not to divulge any secret process, but simply to utilize the information to the advantage of his research or of his knowledge of the subject in general. I believe this scheme was followed in Germany, where every Geheimer Hofrat was given the privilege by law, and where, so far as I know, that privilege was never once abused, though it conduced materially to keeping the universities seats of live learning abreast of the times instead of years behind.

In order to keep our subject before the research men and women of the country I think that we, in the industry, should lose no opportunity of emphasizing the theoretical side of our subject in public by addressing meetings of research men, writing articles, and, if possible, when we know enough about our subject, by writing textbooks or assisting those who wish to do so. You will find, if you think the matter over, that you can discuss most of the theory, even of your most secret processes, without risk of betraying your secret; why not do so instead of getting the schoolman to tell us of the theory apart from our special need?

More than one of the large companies have instituted a system of fellowships and scholarships to keep the subject before the institutions of learning of the country. That is going to help materially, but I have a warning to sound. We must discourage the doing of sporadic work, the making of a color by some novel way. What the universities should do is to contribute to our understanding of the theory, and that they cannot do by building new colored bodies which are very unlikely to succeed as commercial products. The danger is that the problems will be just such as occur to the research chemist in the industry who wonders what would be the result of combining atoms in a new order, but cannot take the time to satisfy his curiosity. The reason why this type of problem will be overdone is that a great many of the men who are in charge of organic work are by no means dye chemists, make no claim to be such, yet they feel that it is only fair to let a student, holding a fellowship given by dye manufacturers, attack a dye problem; they then ask for suggestions and these are given them. What is required is the broadening of our knowledge of the fundamental theories of organic chemistry, and this can be better achieved by systematic work in any chapter of the chemistry of carbon than by the making of odd compounds fashioned on the fancies of the student of applied science.

Just as we do not feel that universities and colleges should attempt technical courses, but train in a knowledge and understanding of the subject, so we wish the contribution of the workers in pure research to be basic. A series of investigations carried out in a logical effort to reach a generalization—that is the type of work that will most benefit the dye industry of this country.

Raw products, money, commercial organization, industrial chemists, all these we may have and yet fail if we have not real research.

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[1] Read at the 59th Meeting of the American Chemical Society, St Louis, Mo., April 12 to 16, 1920.

CHLORINE AS A PREVENTIVE OF INFLUENZA[1]

By Harrison Hale
University of Arkansas, Fayetteville, Arkansas

Received April 1, 1920

By order of the City Board of Health the city schools and churches of Fayetteville, Arkansas, were closed February 1, 1920. It was decided by the authorities of the state university not to suspend university work. Conditions seemed unusually favorable to try the use of chlorine as a preventive of influenza, an indirect report of its preventive influence in the case of employees in a certain government plant during 1918 having been received.

Accordingly one of the smaller chemical laboratories was taken for this work, and daily tests were begun February 2 with volunteers from the college community. The room used was 22 × 15 × 12 ft., and the chlorine was generated by the usual laboratory method of treating manganese dioxide and sodium chloride with sulfuric acid, using 25 to 50 g. of salt in each generator. The amount of chlorine in the air after mixture by an electric fan placed behind the beaker of water through which it was passed to remove excess of hydrochloric acid, varied widely. This showed 43 to 273 parts per million by volume, or 0.011–0.068 per cent by weight as determined by titration with sodium thiosulfate of iodine, liberated when a known volume of air was bubbled through a potassium iodide solution.

This variation was due to differences in the speed at which the gas was liberated and to its removal from the room, through the frequent opening and closing of the door, and by being carried away in the lungs and clothing of those treated. It is also quite certain that the chlorine content at different heights was not the same.

Into this room those receiving treatment came for a period of 5 min., either two or three at the same time, or as many as twenty. Not all took this treatment each day of the eight days upon which it was given. Altogether about 800 treatments were given to 184 different individuals. None of these developed influenza except one, who began to feel sick within a few hours after his first treatment. It seems certain his case had developed before taking the treatment.

Up to February 9 the actual number of cases reported in the town approximated 150, or about one in each 40 inhabitants, but one-third of these developed before the treatments began.

Of the 184 taking the treatment more than two-thirds had had influenza in the attack of a year or more ago. This 184 included six or eight children and several faculty members and was not solely confined to those of college-student age. The nurse who cared for patients at the university infirmary was one of those taking the treatment, and she escaped the disease.

The crowding of a hundred people daily into a small room within a period of the few hours during which treatments were given might have been a source of increased number of cases except for the germicidal effect of the chlorine. Bacterial plates exposed in this room for 10 min. were practically sterile. Similar results, however, were obtained in another laboratory in the same building.

Perhaps two facts should be clearly stated to forestall two false impressions which we encountered: First, the chlorine does not cure after the case is well developed. A few students claimed that it did for them, but their reports are given little credence, as it probably only cleared the nasal passages, and they did not have influenza to begin with; and second, it does not grant future immunity, beyond a very short time.

Our results tend to show that chlorine does act as a preventive of influenza, but the rapid improvement in the local situation, which led to the raising of the quarantine on February 14, prevented their being conclusive. So far as we know this is the first use of chlorine as an influenza preventive in a college community and our results agree with those from chlorine plants as reported by Baskerville[1] a year ago.

Obviously the same treatment could be given in the home, using chloride of lime as the source of the chlorine. There seems to be no danger of causing serious after-effects from too much chlorine, with the amounts we used.

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[1] Presented at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

[1] "Certain War Gases and Health," *Science*, **50** (1919), 50; "Chlorine and Influenza," This Journal, **12** (1920), 293.

CHEMICAL READING COURSES[1]

Prepared by the Committee on the Preparation of a Recommended List of Chemical Texts for Libraries
W. A. Hamor, *Chairman*, L. C. Newell, A. M. Patterson, W. Segerblom

(Concluded from the July issue)

ORGANIC AND BIOLOGICAL CHEMISTRY[2]

"THE DAY" OF THE CHEMIST IS HERE!

What of business in America after the war? Opinion is divided between those who are optimistic and see only continued prosperity, and those who think a period of depression must be weathered. But there is one man who seems sure of a job, and that is the chemist. There is, in fact, not enough of him to supply the demand. The country opened its eyes to him during the war, and now he is needed to solve the economic utilization of our vast resources, the elimination of wastes, improved sanitation, and increase in foodstuffs and clothing.

But it is *trained* chemists that are wanted. There must be thorough preparation for the profession, and those who are prepared must keep mentally alert and in touch with advances in the science.

FIGHTING WITH ORGANIC COMPOUNDS

America would have been at a fatal disadvantage in the World War without her organic chemists. First, they were called on to make good the deficiency in dyes, pharmaceutical products and other items, and new factories sprang up like dream castles. Then came demands for TNT, mustard gas, and other organic tools of war. Truly a wonderful field of knowledge! One of the best known introductions to the subject is Perkin and Kipping's "Organic Chemistry" (New edition; Lippincott, 1917; $2.25[1]). Another clear and interesting book is "The Principles of Organic Chemistry" by J. F. Norris (McGraw-Hill, 1912; $2.50).

HOW THEY ARE MADE

Less than a century ago it was still supposed that organic compounds could be synthesized only by the "vital force" existing in plants and animals, and the artificial preparation of urea by Wöhler in 1828 from inorganic materials is therefore considered an epoch in the history of the science. Since then many other organic compounds have been so made, and a whole host of transformations discovered which can now be carried out by any one with the proper training. F. J. Moore's "Experiments in Organic Chemistry" (Wiley; $0.50) is a widely used little manual requiring only simple equipment. Gattermann's "Practical Methods of Organic Chemistry" is a well tried standard handbook for organic preparations which is available in an English translation (MacMillan, 1916; $1.75).

A HAPPY COMBINATION

The great success attained by Germany in a chemical way was not due, as people now realize, to any inherent superiority in her men, but to the direct encouragement of research by the government, and the close relation between her universities and her manufacturers, all of which resulted in a splendid organization. Pure science and industry have much to gain from intimate association. It therefore seems good fortune to find a book which combines industrial organic chemistry with a discussion of organic theories (E. Molinari, "Treatise on General and Industrial Organic Chemistry," translated by T. H. Pope; Blakiston, 1913; $6.50).

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[1] Presented to the Council at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 2, 1919.

[2] By Dr. Austin M. Patterson

[1] Prices quoted throughout are as of the date of preparation of this report and are printed simply to serve as a guide to the general trend of prices

FOR THE MORE ADVANCED

Those who have advanced a bit into the domain of organic chemistry find themselves in need of a more detailed chart of its complexities. Complete catalogs are very expensive and unfortunately are not yet to be had in the English language, but a comparatively inexpensive reference book, covering the subject in a remarkably thorough way, is available in Victor von Richter's "Organic Chemistry." Vol. I, "Chemistry of the Aliphatic Series" (Blakiston, 1916; $5.00), has been newly translated and revised; the other volume of the English translation is now several years old, but it is still valuable.

An excellent book, which is rather a discussion of important theories than a reference book, is "Organic Chemistry for Advanced Students" by J. B. Cohen (E. Arnold (London), Vol. I, 1909; $7.00; Vol. II, 1913; $4.50).

BASES MADE BY PLANTS

A renowned lecturer on organic chemistry was accustomed to open his concluding discourse by saying, "And now we come to the end—in this case the bitter end—the alkaloids." They are still bitter, but no longer the end, for the proteins, not to be dismissed in a paragraph now, have taken their place there and the relation of the various alkaloids to other organic compounds is now much better understood. "The Plant Alkaloids" by T. A. Henry (Blakiston, 1913; $5.00) is a comprehensive treatment of this subject in English.

THE CHEMISTRY OF LIFE

The chemistry of the living organism, and in particular that of the animal body, has been undergoing a tremendous development. What this means, both in the advancement of the knowledge of chemical compounds and in such practical applications as the prevention and cure of disease, it is possible only dimly to foreshadow. Chemical and biological technique have been invoked together to develop this vitally interesting field. "Physiological Chemistry" by A. P. Mathews (Wood & Co.; $4.25) is a most valuable book, replete with information and written in an entertaining way. A smaller book, of much merit and widely used, is P. B. Hawk's "Practical Physiological Chemistry" (Sixth edition; Blakiston, 1918; $2.50), while S. W. Cole's book of the same title is one of the best laboratory manuals on this subject (W. Heffer & Sons, Cambridge, 1913; 7s. 6d.).

AS SEEN BY A PHYSICAL CHEMIST

It seems that physical chemistry simply will not down. Nor will biological chemists wish it to avoid their field, for it brings to bear on chemical phenomena of all kinds a viewpoint and methods which cannot be neglected. Especially is this true in the hands of such a genius as the Swedish physicist and chemist, Svante Arrhenius. "Quantitative Laws in Biological Chemistry" by this author (Bell & Sons, London, 1915; $2.00) is a most illuminating and stimulating book.

HOW DO ENZYMES ACT?

The mysterious processes of fermentation have long occupied the attention of biological chemists. It was a great step in advance when Büchner isolated zymase in 1897 and demonstrated that the action of "organized" and "soluble" ferments was alike in principle. But that by no means solved the problem. Cohnheim's lectures on "Enzymes" (Wiley, 1912; $1.50) and Euler's "General Chemistry of the Enzymes" (translation, New York, 1912; $3.00) discuss this important class of compounds.

SOME OTHER BOOKS

E. de B Barnett, "The Preparation of Organic Compounds." Blakiston, 1912; $2.75. A book of interest to the research man and works chemist, as well as the undergraduate. The directions are rather brief.

H. F. Clarke, "An Introduction to the Study of Organic Chemistry." Longmans, Green, 1914; $2.00. A straightforward presentation of the principles of the subject, detailed facts being used as illustrations rather than on their own account.

O. Hammarsten and S. G. Hedin, "A Textbook of Physiological Chemistry." Translated from the eighth German edition; Wiley, 1914; $2.00. Was for a long time the chief handbook on the subject and has been well kept up.

J. F. Norris, "Experimental Organic Chemistry." McGraw-Hill; $1.25. Includes a discussion of laboratory methods, preparation of organic compounds, and a study of their properties.

W. A. Noyes, "A Textbook of Organic Chemistry." Second edition, Holt; $1.50. Differs somewhat in its arrangement from the ordinary textbook; theory is given ample consideration.

W. A Noyes, "Organic Chemistry for the Laboratory." Chemical Publishing Co., 1916. Employs practical and typical laboratory methods, with abundant references to the original literature.

R H A. Plimmer, "Practical Organic and Bio-Chemistry." London, 1915, $3.60.

INDUSTRIAL INORGANIC CHEMISTRY[1]

AMERICA AWAKE AT LAST!

Too long has the American manufacturer applied rule-of-thumb methods in his processes, and neglected to regard his procedures in the light of the chemical principles underlying all processes where a change of substance is involved. The employee who familiarizes himself with the essentials of industrial chemistry not only helps his employer but increases his own worth. It needed the Italian Molinari to combine in one volume, "Treatise on General and Industrial Inorganic Chemistry" (Blakiston, 1912; $6.00), enough general chemistry with descriptive accounts of industrial processes to give the reader an intelligent idea of the application of theory to practice. One interested particularly in American methods will find "Industrial Chemistry for the Student and Manufacturer" by Rogers and Aubert (Van Nostrand, 1915; $5.00) unusually attractive. Thorp's "Outlines of Industrial Chemistry" (Macmillan, 1916; $3.25) is a smaller book giving some knowledge of the plants and methods used in the more important manufacturing operations based on chemical changes.

WHAT WOULD WE DO WITHOUT IRON?

Modern industry is based largely on plain, every-day iron. The preparation and behavior of this element vitally concerns many. In his "Blast-Furnace Construction in America" (McGraw-Hill, 1917; $4.00), J. E. Johnson produced an authoritative treatise on American practice in the production of pig-iron, including results of his original investigations. H. M. Howe's "The Metallography of Steel and Cast Iron" (McGraw-Hill, 1916; $10.00), the first volume in a series on the metallurgy of steel, covers microscopic metallography and plastic deformation; it deals not only with the practice of the present but with the possibilities of the future. If iron did not rust how greatly its value would increase! J. N. Friend's "The Corrosion of Iron and Steel" (Longmans, 1911; $1.80) presents a concise account of all important work done on the corrosion of iron, and its numerous references put the reader in contact with all important original contributions to the subject and point the way where further research is necessary. D. K. Bullens' "Steel and Its Heat Treatment" is a practical and easily understood book recommended by the technical press and by authorities throughout the country. An attractive little volume has been written for the lay reader by J. R. Smith. It is called "The Story of Iron and Steel" (D. Appleton and Co., 1908; $0.85) and deals with the economic as well as with the technical side and aims to present the main facts of iron and steel making without the use of technical terms.

IRON NOT THE ONLY METAL

Manufacturing would certainly be a tremendous undertaking if iron were the only metal. Gowland's "The Metallurgy of the Non-Ferrous Metals" (Griffin; $10.00) deals with the extraction of metals in general. Workers in lead should find Hofman's "Metallurgy of Lead" (McGraw-Hill, 1918; $6.00) of interest since it is the latest treatment of this subject and is based on visits to the leading lead plants of the United States and Canada. The same author's "The Metallurgy of Copper" (McGraw-Hill; $5.00) will prove of much value and interest not only to copper smelters but to those engaged in other branches of metallurgy. Americans sometimes fight shy of a book written from the British standpoint and particularly for the benefit of the British reader, but Smith's "The Zinc Industry" (Longmans; $3.50) is free from this suspicion; it is an excellent book and treats the zinc industry of the world in a fairly comprehensive manner. The standard treatise of W. R. Ingalls on zinc and cadmium is, however, the guide of the technologist.

METALLURGY IN GENERAL

A worker in any particular metal can do better work if he has a general knowledge of the other metals. Desch's "Metallography" (Longmans, 1913; $3.00) sets forth very clearly our present knowledge of this subject, which has been defined as the study of the internal structure of metals and alloys and its relation to their composition and to their physical and mechanical properties. Hofman's "General Metallurgy" (McGraw-Hill; $6.00) treats in a scholarly manner the subsidiary branches which are usually slighted or ignored entirely.

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[1] By Mr. Wilhelm Segerblom.

VITRIOL, SALT, ETC.

It is often said that the progress of a nation is measured by its production of sulfuric acid. The point of this statement is appreciated when the extensive use of oil of vitriol in numberless industries is considered. Any good descriptive textbook will present the methods of manufacture, but Sullivan's "Sulphuric Acid Handbook" (McGraw-Hill, 1918; $2.50) will be found to give unusually complete sulfuric acid tables adopted by the Manufacturing Chemists' Association of the United States, arranged for quick reference and for convenient use. Of course, Lunge's "Manufacture of Sulphuric Acid and Alkali" (Van Nostrand, 1917; $43.00) is the standard and rather voluminous authority. Calvert's "Manufacture of Sulphate of Ammonia" (Benn Brothers, 1917; $3.00) describes plants, apparatus, and practice prevailing in Great Britain for making this important salt, largely a by-product of the destructive distillation of bituminous substances.

GLASS AND CERAMICS

The Germans pretty nearly "had us" in the recent war in the matter of optical glass, but American chemists immediately got busy and the German glass secrets remained secrets no longer. Dillon's "Glass" (Putnams, 1907; $7.50) is a descriptive history of glass from the earliest times to the present day. J. W. Mellor, a most entertaining British writer on chemical subjects, has made an important contribution to chemical literature in his "Treatise on the Ceramic Industries" (Griffin and Co., 1913; $7.50).

CEMENT AND UP-TO-DATENESS

Where would modern building be without the use of Portland cement? Its strength is well known but the artistic possibility of cement construction will be better appreciated when this nation stops being in such a hurry and has an eye for beauty as well as utility. Brown's "The Portland Cement Industry" (Van Nostrand, 1917; $3.00) is a practical treatise of the building, equipping, and economical running of a Portland cement plant; it gives probably the most comprehensive review of the entire process of cement manufacture to be found in any book. Taylor and Thompson's "Concrete, Plain and Reinforced" (Wiley, 1917; $5.00) in a recently revised edition treats reinforced concrete from the point of view of theory, design, and tests.

FUELS, COAL AND GAS

The high cost of coal during the recent war has focused much thought on the economical production of heat and energy from the dollar-a-day man to the international manufacturer. Herington's "Powdered Coal as a Fuel" (Van Nostrand, 1918; $3.00) is the only American work on the subject, and considers proper coals, pulverizing, and burning. Those who have to be content with substitutes will find the latest researches on coal and on fuels which have to a great extent replaced or supplemented coal discussed in Poole's "The Calorific Power of Fuels" (Wiley, 1918; $3.00). Perhaps an intelligent conception of methods of making gas in the standard types of apparatus usually found in gas works will make the consumer appreciate better this household convenience; such description is clearly and simply put forth in Russell's "Operation of Gas Works" (McGraw-Hill, 1917; $2.00). It is to the shame of American industry that in one part of the country coal has been distilled for the sake of the coke, allowing the gas to go to waste, while in other parts coal has been distilled for the sake of the gas with the coke as a waste product. Let us hope that modern efficiency methods have put an end to such wasteful practices. Christopher's "Modern Coking Practice" (Crosby Lockwood, 1917; 7s. 6d.) presents a serviceable epitome of the principles and practice of the coking of coal for metallurgical uses.

STRIKING OIL

That reader will "strike oil" who picks up Bacon and Hamor's "American Petroleum Industry" (McGraw-Hill, 1916; $10.00), for this set covers thoroughly the chemistry, geology, technology, history, and economics of petroleum; it is an American treatment of an American industry, modern, comprehensive, and authoritative. Those interested in Russian oil fields will find Thompson's "Oil Fields of Russia and the Russian Petroleum Industry" (Van Nostrand, 1904; $7.50) interesting, voluminous, and well illustrated. Abraham's "Asphalt and Allied Substances" (Van Nostrand, 1918; $5.00) covers the occurrence, modes of production, uses, and methods of testing asphalts. This book is interesting alike to the technical man and to the practical man engaged in the manufacture and sale of products involving the use of bituminous materials.

PAINTS

Maximilian Toch has long been considered an authority on paint. His "Chemistry and Technology of Paints" (Van Nostrand, 1916; $4.00) is a standard work on this subject.

TNT AND ITS RELATIVES

How glibly we have talked lately of TNT as if it were some familiar article of temporary interest. Its chemistry, however, is not so simple. Smith in his "TNT and Other Nitrotoluenes" (Van Nostrand; $2.00) has brought together and correlated all accessible information on the subject, both theoretical and practical. Weaver's "Notes on Military Explosives" (Wiley, 1917; $3.25) is an essentially American book giving a general knowledge of modern explosives, with composition, manufacture, and methods of handling. One who wishes something more voluminous should consult Marshall's "Explosives, Their Manufacture, Tests, Properties and History" (Blakiston, 1917; $16.00). That work covers every topic with fullness and cites original authorities with accuracy.

COLLOIDS AGAIN

Some years ago a boy whose duty it was to tend the churn would surreptitiously drop in a little salt when his mother was not looking because "the butter came better;" at that time he knew nothing of the "colloids" of the process, but he has since become an authority on colloids. Zsigmondy and Spear's "The Chemistry of Colloids" (Wiley, 1917; $3.00) is an authoritative translation of a German work on colloids with several chapters on industrial colloidal chemistry added by the translator. Readers who have not the time for so large a book will welcome Arndt's "Popular Treatise on Colloids in the Industrial Arts" (Chemical Publishing Company, 1914; $0.75).

TOEING THE MARK

War conditions and post-war conditions have made chemistry more than ever such a progressive science that a textbook becomes out of date almost over night. It is absolutely necessary for one wishing to keep in touch with the latest in chemical research to have access to reliable chemical periodicals. Undoubtedly the most valuable encyclopedia of technical chemistry is the *Journal of the Society of Chemical Industry* (published by the Society in London, England; $11.00 per year). This periodical, published semi-monthly, brings in each issue about 100 pages of records of all important work and news connected with chemical industry. *Chemical and Metallurgical Engineering* (McGraw-Hill Co.; $3.00) is an excellent weekly periodical covering somewhat similar, though more restricted, ground for America. It contains many articles suitable for the general reader as well as for the technologist. The *Journal of Industrial and Engineering Chemistry* (published by the American Chemical Society; $6.00) is a 100-page monthly periodical devoted principally to the interests of industrial chemists. The passing of the old idea of secrecy in American chemical industry has brought to the pages of this journal papers of the utmost importance. *Chemical Abstracts* (American Chemical Society; $6.00) is a semi-monthly periodical giving brief, carefully classified abstracts of all important new work in chemistry published in the world. As over 600 journals are abstracted, it is the last word on latest research. (Members of the American Chemical Society obtain the two periodicals last mentioned together with the monthly *Journal of the American Chemical Society*, containing original articles of a more theoretical nature, in return for the annual dues of $10.00.)

SOME OTHER BOOKS

GENERAL

H. K. Benson, "Industrial Chemistry for Engineering Students." Macmillan, 1913; $2.00. Discusses, with latest data, the manufacture, properties, and uses of various materials.

A. Rogers, "Elements of Industrial Chemistry." Van Nostrand, 1916; $3.00. A condensation of "Industrial Chemistry" by Rogers and Aubert.

Society of Chemical Industry, "Reports of the Progress of Applied Chemistry." Includes under different divisions brief reviews and complete bibliographies of all important articles and books published during the year. Three volumes, 1916–18, have appeared to date.

T. E. Thorp, "A Dictionary of Applied Chemistry." Longmans, Green and Co. 5 volumes. $13.50 per volume. Revised 1912–13. Standard reference work in English on chemical technology because most comprehensive and complete. Quite uniformly up-to-date, since all five volumes appeared within two years.

METALLURGY

A. O. Backert, "The A. B. C. of Iron and Steel with a Directory of the Iron and Steel Works and Their Products of the United States and Canada." Denton Publishing Co.; $5.00. A valuable reference work.

J. E. Johnson, "Principles, Operation and Products of the Blast-Furnace." McGraw-Hill, $5.00. An adequate supplement to the same author's "Blast Furnace Construction in America." A valuable work combining theory and practice, with considerable attention to commercial features.

Rodenhauser and Schoenawa's "Electric Furnaces in Iron and Steel Industry." Wiley, 1917; $3.75. A useful book for the furnace builder, the student, or any one interested in electric furnaces for the production of iron and steel.

A. W. Brearley and H. Brearley, "Ingots and Ingot Molds." Longmans, Green, 1918; $5.50. Deals with crystalline structure, shrinkage, contraction cavities, casting temperatures, ingot molds, methods of casting, sound ingots, blow holes, segregation, slag occlusions, and influence of ingot defects on forged steel.

S. Bradley, "The Metallurgy of Iron and Steel." McGraw-Hill; $3.00. Standard both in the educational field and as a handy reference guide for men engaged in the manufacture of steel.

A. Sauveur, "A Metallography and Heat Treatment of Iron and Steel." Sauveur and Boylston, 1918; $6.00. An interesting, practical, and useful book.

A. S. Cushman and H. A. Gardner, "The Corrosion and Preservation of Iron and Steel." A modern work.

H. F. Little, "Aluminium and Its Congeners." Lippincott, 1918; $5.00.

E. S. Mead, "The Story of Gold." Appleton, 1908; $0.85. Deals with the gold-mining industry and the connection between its development and the ebb and flow of business prosperity. Well illustrated and attractively written.

L. DeLaunay, "The World's Gold." Putnam, 1908; $2.00. Treats of the geology, geographical distribution, extraction, and political economy of gold.

O. Hofmann, "Hydrometallurgy of Silver." Hill Publishing Co., 1907; $4.00. Pays particular attention to chloridizing, roasting of silver ores, and the extraction of silver by hyposulfite and cyanide solutions.

W. Rosenhain, "Metallurgy· An Introduction to the Study of Physical Metallurgy." Van Nostrand, 1915; $3.50. The first section of the book deals with the structure and constitution of metals and alloys, the second with the properties of the metals as related to their structure and constitution.

E. E. Thum, "A Practice Book in Elementary Metallurgy." Wiley, 1917; $2.75. Treats of the metallic materials of engineering construction, how they are obtained from nature, and how their properties adapt them to their various uses.

A. W. Fahrenwald, "Cyanide Process." Wiley; $2.00. The object of this book is to furnish a laboratory guide, both for investigating a new ore and for conducting the laboratory of an operating mill.

G. A. Roush and A. Butts, "The Mineral Industry." McGraw-Hill, 1918, $10.00. An exhaustive review, not only of a statistical but of a general nature. Very full and authoritative; indispensable for every metallurgist, mining engineer, and chemist. It is revised annually.

H. A. Megraw, "The Flotation Process." McGraw-Hill, 1918: $3.50. A clear discussion of the flotation process, the most modern form of ore concentration covering both its theory and application.

T. A. Rickard, "The Flotation Process." Mining and Scientific Press; $2.00. This is a useful collection of papers on the practice and theory of the flotation process, published originally in "The Mining and Scientific Press."

R. B. Leighou, "Chemistry of the Materials of the Machine and Building Industries." McGraw-Hill, 1917; $3.00. A well illustrated book dealing with the chemical properties of materials used in building construction and equipment and in machinery construction and operation. Covered clearly from the point of view of the user.

Ceramics and Cement

J. Gruenwald, "Raw Materials for the Enamel Industry and Their Chemical Technology." Lippincott, 1915; $2.75. An American translation of a volume dealing with the sources and methods of preparation of the many constituents entering into the composition of enamels, such as clay, quartz, feldspar, etc.

R. K. Meade, "Portland Cement, Its Composition, Raw Materials, Manufacture, Testing and Analysis." Chemical Publishing Company, 1911; $4.50

Fuels

F. H. Wagner, "Coal and Coke." McGraw-Hill, 1916; $4.00. A treatise giving in concise form data covering various systems of coal carbonization.

F. H. Wagner, "Coal Gas Residuals." McGraw-Hill, 1918; $2.50. A treatise giving the modern methods of securing the residuals pertaining to the carbonization of coal. It has valuable data and diagrams for gas companies and chemical manufacturers.

A. R. Warnes, "Coal-Tar Distillation." Van Nostrand, 1918, $5.00. A British book, primarily for the chemist. It treats of the working-up of tar products.

G. Lunge, "Coal-Tar and Ammonia." Van Nostrand, 1916; $18.00. Contains an enormous mass of information collected by the author on visits to factories, through private correspondence, and from numerous books and periodicals.

M. N. Latta, "American Producer Gas." Van Nostrand, 1910, $6.00. A manual of producer-gas engineering practice suitable for engineer, operator, and promoter.

J. S. S. Brame, "Fuels, Solid, Liquid, and Gaseous." Longmans, Green, 1914; $3.50. This book aims to place before the technical man who is not a fuel specialist a good general knowledge of all fuels of importance.

Petroleum

A. Campbell, "Petroleum Refining." Griffin, 25s.

A. B. Thompson, "Oil-Field Development and Petroleum Mining." Van Nostrand, 1917; $7.50. A practical guide to the exploration of petroleum lands.

D. Hager, "Oil Geology." McGraw-Hill; $2.50. Presents a clear, concise and practical discussion of the occurrence of oil and of its extraction.

C. Richardson, "Asphalt Construction for Pavements and Highways." McGraw-Hill, 1913; $2.00. A pocket-book for engineers, contractors, and inspectors.

Explosives

E. D. S. Colver, "High Explosives." Van Nostrand; $20.00. This treatise contains a mass of information collected from numerous sources and should prove of value to chemists interested in the manufacture, handling and testing of explosives, their raw materials and intermediates.

Brunswig's "Explosives." Wiley, 1912; $3.00. This book gives a synoptic and critical treatment of the literature of the subject as gathered from various sources and presented for convenient reference.

Colloids

W. Ostwald, "Theoretical and Applied Colloid Chemistry." Wiley, 1917; $2.50. A series of lectures delivered in America in 1913–14; gives a general survey of modern colloid chemistry.

Miscellaneous

Underwood and Sullivan, "Chemistry and Technology of Printing Inks" Van Nostrand, 1915; $3.00. Brief and practical. Treats of raw materials and finished products.

L. B. Lockhart, "American Lubricants from the Standpoint of the Consumer." Chemical Publishing Company, 1918; $2.00 An important addition to the scanty literature of the subject. Aims to aid the user and buyer of lubricants to a more intelligent selection of oils and greases.

T. Koller, "Utilization of Waste Products." Scott, Greenwood and Son; 12s. 6d. A treatise on rational utilization, recovery and treatment of waste products of all kinds.

A. Vosmaer, "Ozone, Its Manufacture, Properties and Uses." Van Nostrand, 1916; $2.50. A scientific and accurate book.

H. E. Williams, "Chemistry of Cyanogen Compounds." Blakiston, 1915; $3.50. The author has compiled practically all the information available on cyanogen compounds and has used judgment in his composition.

S. J. Levy, "The Rare Earths." Longmans, Green, 1915; $3.00. A fairly comprehensive account from the chemical point of view.

L. Derr, "Photography for Students of Physics and Chemistry." Macmillan, 1906; $1.40. Treats of the general principles and processes of photography. Designed for those who are interested in reasons as well as results.

A. M Patterson, "A German-English Dictionary for Chemists." Wiley 1917; $2.00. This book contains over 30,000 definitions and includes terms of all branches of chemistry and the various chemical industries, and such terms from allied sciences as are likely to appear in chemical literature.

R. B. Pilcher and F. Butler-Jones, "What Industry Owes to Chemical Science." Van Nostrand, 1918; $1.50. A series of articles written for the educated public and showing how various industries were advanced by a knowledge of chemistry.

"The Chemical Engineering Catalog." The Chemical Catalog Company, 1919; $5.00. A compilation, primarily for chemical engineer, superintendent, and buyer, containing information regarding chemical-technical data, plant equipment and products, and sources of supplies for laboratory and works. It is published annually and serves a highly useful purpose.

INDUSTRIAL ORGANIC CHEMISTRY[1]

FORWARD MARCH WITH THE CHEMISTS

What a picture dyes, drugs, TNT, and foods bring up! How dependent America was at her entrance into the war and how bravely she met the crisis! To many the intricacies of organic Chemistry are worse than Greek, but much credit is due Molinari, who, in his "Treatise on General and Industrial Organic Chemistry" (Blakiston, 1913; $6.00), did much to clarify the complexity of organic substances. This comprehensive work classifies the organic compounds in the usual way, according to their structural formulas, but pays special attention to and treats in much detail the industrial side. It differs from most organic texts in that it pays less attention to the theoretical and systematic exposition and more to industrial applications.

THE MOST VITAL QUESTION—FOODS

The present and future generations are much indebted to pure food agitation and every householder should have a slight knowledge, at least, of the chemistry of foods. Bailey's "Source,

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[1] By Mr. Wilhelm Segerblom.

Chemistry and Use of Food Products" (Blakiston, 1916; $1.60) discusses the source, preparation for the market, packing, preserving, shipping, composition, nutrient, and dietetic value of foods and drinks used by people of different countries. H. W. Wiley, long in the American public eye because of his earnest work in establishing pure food legislation, has described the origin, manufacture, and composition of food products, and has written on food standards and the detection of common adulterations in a large and attractively illustrated volume called "Foods and Their Adulteration" (Blakiston, 1918; $4.00).

WATER, SEWAGE AND SANITATION

When New York City can spend two hundred million dollars on the installation of a water-supply system that will furnish sufficient pure water for that metropolis to forestall any danger of water famine, it is evident that other cities should not neglect this most important side of existence. Ellm's "Water Purification" (McGraw-Hill, 1917; $5.00) gives a comprehensive treatment of the whole subject of water purification by a man widely known and closely identified with water supply and purification for many years. It includes the design, construction, equipment, and operation of filtration plants. Up-to-date water departments practice the German art of "gassing," but they do it against the millions of germs and they do it by means of chlorine. Race's "Chlorination of Water" (Wiley, 1918; $1.50) presents in a comprehensible manner information on methods of chlorination hitherto scattered in various journals.

BACK TO THE SOIL

If the cycle of nitrogen, of phosphorus, and of carbon in nature were better understood, the landscape would be deprived of many abandoned farms. Stoddart has written a text called "Chemistry of Agriculture" (Lea and Febiger, 1915; $2.00), which covers the subject briefly. Students of practical agriculture who wish to get enough chemical instruction to understand the problems of agricultural practice will find Chamberlain's "Organic Agricultural Chemistry" (Macmillan; $1.60) useful. With the artificial production of fertilizers has come much talk about cyanamide; Pranke's "Manufacture, Chemistry, and Uses of Cyanamide" (Chemical Publishing Company; $1.25) will clear up much ignorance on this subject.

CELLULOSE AND PAPER

Thomas Churchyard, when describing a paper mill of the 14th century, wrote:

> I prayse the man that first did paper make
> The only thing that sets all virtues forth;
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> * * * * *
>
> Without whose help no hap nor wealth is won,
> And by whose ayde great works and deedes are done.

R. W. Sindall in "Manufacture of Paper" (Van Nostrand, 1913; $2.00) sets forth interestingly the various stages of the manufacture of paper. Numerous halftones and a full bibliography enhance the value of the book. A practical treatise on the reworking of old or waste papers is Strachan's "Recovery and Re-manufacture of Waste Paper" (Albany Press, 1918; 12s. 6d.). This book is produced on a reworked paper as the best possible illustration of the subject matter.

DYES AND TEXTILES

The coming of the "Deutschland" did not succeed in holding the American market for German dyestuffs. About 175 dyes are now being made in the United States from American raw materials and intermediates; these products equal in shade, strength, and working qualities those of the pre-war types, and include members of all groups of colors formerly used in American mills. The present dye situation is well put forth in the address delivered by J. H. Choate, Jr., of the Alien Property Custodian Office before the AMERICAN CHEMICAL SOCIETY, and printed in the May 1919 number of the *Journal of Industrial and Engineering Chemistry*. A book which covers practically the whole scientific literature of colors with results of investigations not before published is Perkin and Everest's "Natural Organic Coloring Matters" (Longmans, Green; 28s.). Barnett's "Coal-Tar Dyes and Intermediates" (Baillière; 10s. 6d.) is written with a free hand, is exceedingly timely, and is full of concise information on methods of large-scale operations. A book on textiles adapted to a wide range of readers is Woolman and McGowan's "Textiles" (Macmillan, 1916; $2.00). It aims to give a sound grasp of the subject with so much of the technology as is directly helpful to the consumer.

OILS, FATS, ETC.

A complicated and rather illusive subject is covered by Wright and Mitchell in their "Animal and Vegetable Fixed Oils, Fats, Butters, and Waxes" (Lippincott, 1903; $8.00). This book describes methods whereby animal and vegetable oils and fats are obtained from natural sources, their practical applications and uses, also their chief physical and chemical properties and reactions. A new industry is discussed by Carleton Ellis in his "Hydrogenation of Oils" (Van Nostrand, 1919; $4.00). This book reviews the chemistry of fats and gives in logical order all known facts and figures of this new branch of technical chemistry.

LEATHER AND GLUE

Temporary roads may well have been made from old shoes, as was the case in the war zone, but other uses will probably occupy the attention now. Flemming's "Practical Tanning" (Baird, 1916; $6.00) is a handbook of modern processes, receipts, and suggestions for the treatment of hides, skins, and pelts of every description.

RUBBER

With only one set of pneumatic tires available in Germany during the war, rubber substitutes were naturally in order. Porritt in his "Chemistry of Rubber" (Van Nostrand, 1914; $0.50) has produced an admirable, briefly written review of the status of the rubber industry up to the time the book was printed.

OTHER BOOKS

General

S. P. Sadtler, "Industrial Organic Chemistry." Lippincott, 1912. $5.00. Adapted for the use of manufacturers, chemists, and all interested in the utilization of organic materials in the industrial arts.

Foods

R. N. Hart, "Leavening Agents." The Chemical Publishing Company; $1.00. Yeast and baking powders are briefly discussed from the manufacturer's point of view.

C. A. Mitchell, "Edible Oils and Fats." Longmans, Green; $2.00. In this valuable and useful little volume is given a concise outline of the chemical composition and properties of the more important oils and fats, together with a description of the methods of their extraction from the crude materials and of their purification for use as foods.

H. C. Sherman, "The Chemistry of Food and Nutrition." Macmillan; $2.00. This book presents the principles of the chemistry of foods and nutrition, with specific reference to the food requirements of man.

J. Grant, "Chemistry of Bread Making." Longmans, Green, 1917, $1.40. A textbook on the application of physics and chemistry. It treats also of the large-scale use of meals, flours, cereals, yeast, etc.

H. W. Conn, "Bacteria, Yeasts, and Molds in the Home." Ginn, 1912; $1.00. Of interest not only to students of household economics, but to all persons having practical charge of homes.

E. O. Jordan, "Food Poisoning." University of Chicago, 1917. Concise, authoritative, non-technical summary of present-day knowledge of poisons, bred in, added to, or naturally found in foods.

H. Classen, "Beet Sugar Manufacture." Wiley, 1910; $3.00. A book for technical sugar men on the more important operations in a sugar factory.

H. C. P. Gurligs, "The World's Cane Sugar Industry, Past and Present." Van Nostrand, 1912; $5.00.

Water and Sanitation

W. P. Mason, "Water Supply." Wiley, 1916; $3.75. The new edition has brought data in regard to water supply, primarily from the sanitary standpoint, down to date.

W. W. Christie, "Water, Its Purification and Use in Industries." This book contains general information regarding water, together with tables of value to users of water for manufacturing and industrial purposes.

Kinnicutt-Winslow-Pratt, "Sewage Disposal." Wiley, 1919; $4.00. A revision of a work long standard, brought down to date by chapters on two-story tank treatment, treatment by means of activated sludge, and other new phases of sewage disposal and purification.

Soils

T. L. Lyon, "Soils and Fertilizers." Macmillan, 1917; $1.10. This book, intended for use in secondary schools, is clearly and well written and presents fertilizing from the standpoint of intensive agriculture.

Cellulose and Paper

T. C. Chaudhuri, "Modern Chemistry and Chemical Industry of Starch and Cellulose." Butterworth and Co., 1918; 3s. 12d. Aims, to give a brief survey of the various chemical industries directly or indirectly bearing on starch and cellulose, especially in the light of recent research.

E. C. Worden, "Technology of Cellulose Esters." Van Nostrand, 1916; $50.00. In 10 volumes the author presents the combinations of cellulose with acid radicals in such completeness that inability to find the information sought will be evidence that it is non-existent or of no value.

E. C. Worden, "Nitrocellulose Industry." Van Nostrand, 1911; $10.00. The most complete and comprehensive work on the general technology of nitrocellulose ever issued in any language; it covers the entire field adequately and in detail, containing over 8000 references to patent and research literature.

Dyes and Textiles

Beacall, Challenger, Martin, and Sand, "Dyestuffs and Coal-Tar Products." Appleton, 1915; $2.75. A collection of articles on coal-tar products, synthetic dyestuffs, dyeing and printing industry, inks, synthetic drugs and photographic chemicals, selected largely from a larger book by one of the authors.

J. C. Cavin, "Manufacture of Intermediate Products for Dyes." Macmillan, 1918; $3.50. Aims to present the literature of intermediates in a sufficiently complete form so that the interested chemist can base his work on the descriptions given without reference to the original literature.

I. W. Fay, "The Chemistry of Coal-Tar Dyes." Van Nostrand, 1911; $4 00. Intended for those dyers who have a good knowledge of general chemistry and some knowledge of organic chemistry. Methods of making and relation between the classes of dyes are also considered.

S. H. Higgins, "Dyeing in Germany and America." Longmans, Green; 5s. A general survey of the dyeing and allied industries of the United States and Germany prepared from material collected during a tour of these countries in 1905 and 1906.

J. M. Matthews, "The Textile Fibres." Wiley, 1904, $4.00. Large and technical, but contains chapters of interest to the general reader. All facts concerning textile fibers, their physical, microscopic, and chemical properties are systematically presented.

Oils, Fats, Etc.

D. Holde, "Examination of Hydrocarbon Oils and of the Saponifiable Fats and Waxes." Wiley, 1915; $5.00. This book contains much valuable descriptive information not found elsewhere.

Leather

A. Watt, "Leather Manufacture." Van Nostrand, 1906; $4.00. A practical handbook of tanning, currying, and chrome-leather dressing. Very instructive and helpful text, not only for chemists and manufacturers of leather, but also for the general reader.

Rubber

A. Heil, "Manufacture of Rubber Goods." Lippincott, 1909; $3.50. A practical handbook for the use of manufacturers and chemists.

H. C. Pearson, "Rubber Machinery." India Rubber World, 1915; $6.00. An encyclopedia of machines used in rubber manufacture.

C. O. Weber, "Chemistry of India Rubber." Lippincott, 1903; $5.50. A standard work including the outlines of a theory on vulcanization.

TECHNO-CHEMICAL ANALYSIS[1]

BETTER THAN THE CHANCE OF A LIFE-TIME

An office boy can be taught to remove a beaker from a steam bath at the proper moment, and he may even be taught how to weigh a sample accurately to the first decimal place, but it takes a chemist with some little knowledge of reactions to select the best method of analysis and to know the right thing to do when the procedure does not go according to rule. Trouble in manufacturing processes is often caused by the use of impure raw materials. "Treatise on Applied Analytical Chemistry" (Blakiston, 1918; $12.00), by Villavecchia, presents those subjects which deal with the purchase of raw material for manufacturing processes; it also gives some attention to the analysis of finished products from the standpoint of impurities and adulterations.

INORGANIC ANALYSIS

A father once came with his boy to a college professor and asked him to teach his boy how to "do copper," but to omit everything else and not to bother about any of the principles of chemistry. Fortunately such misinformation is becoming a thing of the past. No analyst can "do copper" or "do" any other analysis without some knowledge of the general behavior of chemical reagents and the laws underlying such changes. A much used book that deals comprehensively with the fundamental principles of analysis is Treadwell and Hall's "Analytical Chemistry" (Wiley, 1916; $6.50). Volume I treats of Qualitative Analysis and Volume II of Quantitative Analysis.

ORGANIC ANALYSIS

The analysis of organic substances presents peculiar difficulties that cannot be solved by the schemes of analysis associated with inorganic analysis. Arup's "Industrial Organic Analysis" (Blakiston, 1913; $2.25) is a useful work for those practicing chemists who do not possess the more expensive treatises. Of course, Allen's "Commercial Organic Analysis" (Blakiston, 1917; $45.00) stands par excellence as the standard. It is a treatise on the properties, modes of assaying, and proximate analytical examination of the various organic chemicals and products employed in the arts, manufactures, medicine, etc., with concise methods for the detection and estimation of impurities, adulterations, and products of decomposition.

METALLURGICAL ANALYSIS

Since "iron is not iron," that is, since commercial iron is never chemically pure iron, but a mixture of iron with definite percentages of various other elements and occasionally compounds, its technical examination ranks high in importance in industry. Blair's "Chemical Analysis of Iron" (Lippincott, 1918; $5.00) has long been the standard guide, bringing within one volume all the methods of real value to the iron analyst. A book covering a wide field is White's "Methods in Metallurgical Analysis" (Van Nostrand; $2.50). This is an excellent handbook for the commercial analyst as well as the student, because in it are compiled methods used in American metallurgical laboratories.

FOOD ANALYSIS

Pure Food! What is it? Public analysts, health officers, sanitary chemists, and food economists will find Leach's "Food Inspection and Analysis" (Wiley, 1913; $7.50) a standard work. Woodman in his "Food Analysis" (McGraw-Hill, 1915; $3.50) discusses more in detail the analytical processes involved, their suitability and limitations, with emphasis on the interpretation of the analytical results.

WATER

Probably the best book on water analysis is Mason's "Examination of Water" (Wiley; $1.25). As the author deprecates all analytical processes that fail to consider the history and environment of the water, the reader should experience less of the customary difficulty of interpreting results.

GAS ANALYSIS

A complete treatise on gas analysis covering the subject fully and in a way that should greatly help a chemist or engineer interested in the sampling and analysis of gases or fuels is White's "Technical Gas and Fuel Analysis" (McGraw-Hill; $2.00).

DYES

More useful and readily accessible analytical and identification information on coal-tar and other dyes may be found in Green's "The Analysis of Dyestuffs" (Griffin, 1916; $3.00) than in any other recent book. It includes the identification of dyestuffs in dyed and colored materials, lake-pigments, foodstuffs, etc.

PAINTS

Important methods of analysis selected from the laboratories of American manufactories are presented in Gardner and Schaeffer's "Analysis of Paints and Painting Materials" (McGraw-Hill, 1911; $1.50). Correlated with these methods are many that are new and valuable.

OILS

A concise manual for the analysis of the commonly occurring animal, mineral, and vegetable oils is Gill's "Short Handbook of Oil Analysis" (Lippincott, 1918; $2.50). It treats also of the properties, uses, and adulterants of oils.

MISCELLANEOUS

An analytical chemist can hardly get along without a handbook of some kind. Lunge's "Technical Chemist's Handbook" (Van Nostrand, 1917; $3.50) contains analytical factors which have been recalculated on the basis of the atomic weights, published by the International Committee for 1916. Another book of great value is Merck's "Chemical Reagents, Their Purity and Tests" (Van Nostrand, 1914). This handbook treats of the testing of the more common reagents in a satisfactory manner.

OTHER BOOKS

Inorganic and Organic

W. W. Scott, "Standard Methods of Chemical Analysis." Van Nostrand, 1917; $6.00. A compilation of carefully selected methods that have proved of practical value to professional chemists. A book of general reference for the analytical chemist.

S. P. Mulliken, "Methods for the Identification of Organic Compounds by a Systematic Analytical Procedure Based on Physical Properties and Chemical Reactions." Wiley, 1916; $14.00. This work contains classified descriptions of about 2300 of the more important compounds of carbon with hydrogen and oxygen.

S. P. Mulliken, "Methods for the Identification of Pure Organic Compounds." Wiley, 1916; $5.00. Similar to the preceding, but covers about 4000 organic nitrogen compounds.

Metallurgy

H. Fay, "Microscopic Examination of Steel." Wiley, 1917; $1.25. Intended originally for inspectors of ordnance material, but found to be of general usefulness.

C. M. Johnson, "Rapid Methods for the Chemical Analysis of Special Steels, Steel Making, Alloys, and Graphites." Wiley, $3.00. The methods given represent the latest practice and aim at combining speed, simplicity, and accuracy.

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[1] By Mr. Wilhelm Segerblom.

W. B. Price and R. K. Meade, "Technical Analysis of Brass and the Non-Ferrous Alloys." Wiley, 1917; $3.00. The completeness of this book will save the chemist many hours of searching of the literature.

Foods

F. W. Tanner, "Bacteriology and Mycology of Foods." Wiley, 1919; $6.00. Good for those wishing to fit themselves for food control work. Standard methods of Public Health Association freely quoted.

C. A. Browne, "Handbook of Sugar Analysis." Wiley, 1912; $6.00. This book includes the occurrence, methods of preparation, properties, and reactions of the different sugars and their allied derivatives.

F. G. Wiechmann, "Sugar Analysis." Wiley, 1914; $3.00. A standard work.

Gas

L. M. Dennis, "Gas Analysis." Macmillan, 1913, $2.10. This book embodies the results of recent research. Detailed information is given on the collection and storage of gases, the measurement of large gas volumes, the analysis of flue, illuminating and fuel gas, and the determination of the heat value of solid, liquid, and gaseous fuels.

American Gas Institute, "Chemist's Handbook." American Gas Institute; $3.50. The methods given are the official ones of the United States Bureau of Mines and of the American Society for Testing Materials.

Dyes

S. P. Mulliken, "Method for the Identification of Commercial Dyestuffs." Wiley, 1910, $15.00. Those acquainted with Mulliken's other books listed above need no word of commendation here.

Paints

H. Ingle, "Oils, Resins and Paints." Lippincott, $1.25. This book gives in very brief form the whole subject of the analysis of materials of interest to painters.

Oils

J. I. Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes." Macmillan, 1915; $18.50. The last edition of this treatise may well stand for many years as the leading work of reference in its field.

Miscellaneous

J. W. Richards, "Metallurgical Calculations." McGraw-Hill, 1918; $5.00. Contains an enormous mass of data collected and arranged in logical order.

E. M. Chamot, "Elementary Chemical Microscopy." Wiley, 1915; $3.00. This important book outlines the manipulation of the microscope and shows how its use will serve to shorten the work of the analyst and render his results more accurate.

T. F. Hanausek, "Microscopy of Technical Products." Wiley, 1907; $5.00. Shows how to investigate microscopically commercial raw materials with reference to their composition and suitability for technical purposes.

E. L. Smith, "Electro-Analysis." Blakiston, 1918; $2.50. This book brings together material found reliable by the test of experience and embodies latest results.

A. H. Low, "Technical Methods of Ore Analysis" Wiley, 1915; $2.75. This book describes methods suitable for cases most likely to be found in practice.

G. N. Heath, "Analysis of Copper and Its Ores and Alloys." McGraw-Hill, 1916; $3.00. The first connected account of the principal methods employed in the largest refineries and foundries; it follows the ore from the mine to the finished metallic product.

H. W Wiley, "Principles and Practice of Agricultural Analysis." Chemical Publishing Company; $14.50. A manual for the study of soils, fertilizers and agricultural products.

SCIENTIFIC SOCIETIES

CANADA MEETING OF THE AMERICAN INSTITUTE OF CHEMICAL ENGINEERS

In many respects the Canada meeting of the Institute of Chemical Engineers (June 28 to July 3) was the most successful so far held by this Society. The attendance was larger than that of any previous meeting, about 175 throughout the entire week. Interest was maintained not only by unusually excellent papers and visits to plants not commonly seen, but also by the opportunity of seeing some of the most beautiful scenery of the United States and Canada.

The meeting really started when some 60 members, their wives, and guests, boarded the S. S. Berkshire at New York, Saturday evening, June 26, for the sail up the Hudson River to Albany, where special parlor cars had been provided for the rail trip.

The meeting proper was opened at the Hotel Windsor, Montreal, Monday morning, with an address of welcome by City Commissioner R. A. Ross. At the business session the membership was reported as 406, with 30 applications unacted upon. New Orleans was decided upon as the place for the winter meeting, and Detroit for the summer meeting.

President David Wesson addressed the Institute on the qualities essential to a chemical engineer. Prof. A. W. Smith read a paper on the Mann Report in which he pointed out a number of errors in this important study of engineering education, and cautioned the engineers against accepting all of the conclusions of the report without careful criticism.

The symposium on Electrolytic Cells was introduced by Mr. C. B. Barton of the Brown Company who described in a very interesting manner their early development. Mr. Hugh K. Moore discussed the fundamentals of the electrolytic diaphragm cells and the development and performance of the Allen-Moore cell. Mr. L. D. Vorce described the Vorce vertical cylindrical cell, and Mr. A. H. Hooker gave a description with lantern slides of the installation of Townsend cells at the Niagara Falls plant of the Hooker Electrochemical Company. Mr. Hooker also read a paper giving the results of an extended study of the solubility of salt in caustic soda solutions at various temperatures.

Mr. Richard K. Meade gave a very complete description, illustrated with lantern slides, of the manufacture of lime for chemical and metallurgical purposes. The new evaporator laboratory at the University of Michigan was described by Prof. W. L. Badger of the University, who presented three other papers giving the results of studies carried out in that laboratory. Mr. W. D. Richardson read three papers giving the results of a study of the corrosion of a large number of samples of steel.

An excellent review of the progress recently made in the by-product coke oven industry was given by Mr. C. R. Bellamy of the Semet-Solvay Company. Mr. H. O. Chute gave a comprehensive survey of dendro-chemistry, and Mr. E. B. Miller gave the results of commercial experiments on adsorption with silica gel.

On Wednesday afternoon the glycerol refinery of Marx and Rawolle was visited, where glycerol is refined by the Wood multiple effect distillation process. The extensive plant of the Canada Malt Co., Ltd., was also visited, where up-to-date mechanical methods of handling the barley and malt were very much admired.

On Wednesday morning the entire party boarded the special train which had been provided by the Canadian National Railways for the trip to the various centers of Canadian chemical industries.

At Ottawa the party was taken in special cars to the works of the E. B. Eddy Co., manufacturers of sulfite pulp, paper, and indurated fiber products. All parts of the process were inspected, after which an automobile tour arranged by the Board of Trade gave an opportunity for seeing the many beautiful buildings of Ottawa, and the natural beauty of this locality.

Belleville was reached via the scenic Rideau Lake district, and on Thursday morning at 9:30 automobiles were provided by the citizens of Belleville for a drive about the city and a tour to Delora via Sterling and Marmora, viewing en route the beautiful Oak Hills and Trent Valley. Luncheon was served in the Club House by the Delora Smelting & Refining Company, Mr. S. B. Wright, manager of the plant, acting as host and giving a fine address of welcome. The visit to this plant proved very interesting. The separation of cobalt, nickel, iron, and arsenic involved the carrying out on a commercial scale of some complicated chemical reactions. The extensive settling chambers and bag house the for collection of the arsenic fumes were examined with interest, as were the electric furnaces in which the nickel, cobalt, and stellite were melted. The next stop was at the talc mines, and then at the mills of G. H. Gillespie and Co., where the talc was ground in ball mills, air-floated, and passed through screens until it was an impalpable powder. The very extensive industrial alcohol plant at Corbyville was visited, after which the party returned to Belleville to the reception of Mrs. L. E. Allen at the Belleville Club.

In the evening the members of the Institute and prominent citizens of Belleville dined at the Hotel Quinte, with Capt. Lucius E. Allen as toastmaster. With the Stars and Stripes and the Union Jack draped above the speakers' table many references were made to the cordial relations existing between the Dominion of Canada and the United States. President David Wesson especially emphasized this point. Secretary J. C. Olsen told the people of Belleville what a chemical engineer is, although he said this is a much discussed subject.

Dr. S. P. Sadtler, the first president of the Institute, presented the Institute medal to Mr. Hugh K. Moore for the best series of papers presented to the Institute since 1913, when the medal was awarded to Dr. F. W. Frerichs. Mr. Moore responded in a very happy speech, remarking that his papers were so long that they boosted the price of paper. Prof. Chas. Baskerville responded to the toast to the President of the United States.

Lieut. Col. Ponton spoke very effectively on "The City of Belleville and the County of Hastings," pointing out that it was very appropriate that on Dominion Day citizens of the Great Republic and the great Dominion should celebrate the day together.

The party proceeded by special train to Shawinigan Falls where the very extensive power development was first visited. The plant of the Canada Carbide Company was also inspected. The 40-ton continuous calcium carbide furnace was observed with very great interest. At the plant of the Canada Electrode Company the process of making the enormous electrodes for the carbide furnaces was shown. The manufacture of acetaldehyde and acetic acid from acetylene was seen at the plant of the Canadian Electro Products Company. The last concern visited at this point was the unusually well managed plant of the Belgo-Canadian Pulp and Paper Company.

The following morning the party arrived at LaTuque where the enormous pulp mill of the Brown Company was visited. Here the greatest interest was shown in the Moore process for the evaporation and combustion of the black liquor.

The lumbermen's dinner served at Sorting Gap proved the most novel feature of the entire meeting. The songs of the lumbermen, as well as the log rolling, log race, boat race, and log chopping contests will never be forgotten by those who enjoyed this novel entertainment.

Further opportunity to see the numerous lakes and timber lands of Canada was given on the trip to St. Alphonse, HaHa Bay, where the party boarded the S. S. Saguenay for the sail down the broad, deep river flowing between immense masses of rock. The sail on the St. Lawrence to Quebec proved equally interesting. One hundred of the party stopped at the Chateau Frontenac and visited the beautiful and historic city of Quebec, and then scattered for the trip home. The meeting was conceded by all to have been the most profitable, entertaining, and best attended meeting ever held by the American Institute of Chemical Engineers. J. C. Olsen, *Secretary*

Polytechnic Institute of Brooklyn
Brooklyn, N. Y.

IMPROVEMENT OF CONDITIONS FOR COLLEGE INSTRUCTING STAFFS

At the meeting of the Council of the American Chemical Society in St. Louis, April 12, 1920, a committee was appointed to draw up resolutions covering the status of college professors, with particular reference to salaries, and the great difficulty now experienced in securing a proper teaching staff. The resolutions submitted by the committee, William McPherson, *chairman*, follow:

> The American Chemical Society, representing over 15,000 American chemists, having at heart the welfare of our country and desiring to lend every aid possible in the solution of the weighty problems of reconstruction now before our people, respectfully desires to call the attention of those in authority in our colleges and universities, to a condition of affairs which the Society views with grave apprehension.
>
> While the fundamental importance of chemistry has long been recognized it required the experiences of a world war to really arouse the nation to a full sense of the vital character of the science. As a result, the demand for thoroughly trained chemists is unprecedented and far exceeds the supply. The disturbing factor, however, is that the high salaries offered by the industrial organizations and the correspondingly low salaries paid by most of our colleges and universities are tempting men away from our educational institutions, with the result that the teaching profession is being robbed of many of its best members. This process has already progressed to a serious extent and if allowed to continue the results will be disastrous; for it will mean that our future chemists who must play such an important part in the development of our nation will be trained more and more largely by incompetent teachers.
>
> Because of these facts, the American Chemical Society most respectfully urges those in authority in our colleges and universities to do everything in their power to retain the services of such members of the instructional staff of their Departments of Chemistry as are recognized leaders of their profession and to make adequate provisions for the training of the younger members of such staffs so as to insure a continuous supply of competent teachers. To accomplish these results the following steps will be necessary.
>
> (*a*) The salaries of the members of the instructional staff of the colleges and universities must be raised until, taken in conjunction with the privileges which belong to academic life and associations, they offer attractions comparable with those paid by industrial firms. At present our most competent teachers of chemistry are receiving on the average certainly not more than half the salary they could obtain in the industries. Our graduates immediately upon leaving their Alma Mater are, as a rule, paid salaries in excess of competent assistants and instructors and it is a very common occurrence for a graduate who has been out of college for only four or five years to be receiving a salary in excess of those paid his former professors who have given years to their work and are leaders in their profession.
>
> (*b*) Adequate provisions must be made so that members of the instructional staff of the Departments of Chemistry may have ample time and provision to carry on research work. At present many of our educational institutions require of a staff so much time for teaching as to leave little opportunity for study and research. Moreover, it seems to be very generally true that our professors of chemistry have developed qualities that make them efficient members of committees and the time thus spent in committee work still further diminishes the time available for research. Such a state of affairs is absolutely fatal for no instructor can develop in his field of study unless given the opportunity to carry on research work, and no professor can retain his enthusiasm as a teacher and his ability to train students in fields of investigation unless he himself has ample opportunity to devote to the study of new problems.
>
> The American Chemical Society most respectfully solicits your interest in the above matters to the end that our future chemists may be trained by leaders in the chemical profession.

Copies of these resolutions, which were sent out to college and university presidents, have met with a very hearty response. A portion of the reply of President Stone, of Purdue University, which states the situation clearly, is here quoted:

> The growing practice of private corporations in calling scientific men from our institutions in order to conduct research in the interest of some particular line of industry is in my judgment to be severely condemned. In so doing these private

concerns withdraw from public service our best trained men, secluding them in the interests of private business. Nothing could be more short-sighted even for the industry itself than this way of monopolizing men for private gain.

A teacher or an investigator in a public institution multiplies himself a thousand fold for the benefit of all the people and all the industries. In the employ of a private corporation his efforts are limited and the results of his work restricted to the use of his employer. In the long run, industries will best profit by supporting the work of these men in a public way in all institutions where they are free to teach and investigate without restriction.

In this connection it is interesting to note that the same subject is receiving serious consideration in England. At the recent annual conference of the British Association of Teachers in Technical Institutions a similar resolution was adopted, urging the immediate adoption of a suitable scale of salaries, and the placing of every teacher at the point on the scale which he would have reached had it been in operation over the whole of his teaching service.

SIXTH NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES

Reports of progress in the preparations for the Exposition, received since the publication of the June issue of THIS JOURNAL, still further indicate a most valuable and unusual exhibition, from the standpoint of both chemist and manufacturer.

There have so far been arranged four symposiums, on Fuel Economy, Industrial Management, Chemical Engineering, and Materials Handling. For the last mentioned, no papers have been announced, with the exception of "Chain Belt Transmission," by F. G. Anderson. The programs for the others are in part as follows:

FUEL ECONOMY

Fluid Heat Transmission. A. B. MCKECHNIE, Parks-Kramer Co.

Refractory Cement: Life Insurance for a Furnace. F. W. REISMAN, Quigley Furnace Specialties Co.

Producer Gas and the Modern Mechanical Producer. W. B. CHAPMAN, Chapman Engineering Co.

Preventing Conduction and Radiation Heat Waste. S. L. BARNES, Armstrong Cork Co.

Powdered Coal. W. O. RANKIN, Quigley Furnace Specialties Co.

INDUSTRIAL MANAGEMENT

Ultra Analysis of Costs. HARRINGTON EMERSON.

Research in Industrial Conservation. H. E. HOWE, National Research Council.

CHEMICAL ENGINEERING

Construction of Horizontal Stills. A. HOUGH AND WALLACE SAVAGE.

New Method of Destructive Distillation. THOMAS W. PRITCHARD.

Corrosion and Galvanic Action in the Industries. W. D. RICHARDSON.

Among the motion picture films illustrating various industries are the following:

U. S. CHEMICAL INDUSTRIES SERIES

The Story of Sulfuric Acid. General Chemical Co.

A New Chemical Industry—Leather from the Sea-Fish Leather. Ocean Leather Co. (Ford Educational Film Co.).

Perfumes for the World. Antoine Chiris Co.

Modern Coke and Gas Manufacture. The Koppers Co

The Story of Petroleum Oil. Standard Oil Co. of N. J.

The Asphalt Paving Industry. Barber Asphalt Paving Co.

Colloidal Movement in Asphalt. Barber Asphalt Paving Co.

MINING INDUSTRIES SERIES

The Production of Salt for the Chemical Industry. International Salt Co.

The Story of Coal. Sullivan Machinery Co. and U. S. Bureau of Mines.

Building, Mining, and Quarrying Machinery. Sullivan Machinery Co

Silver Mining in Ontario. Ontario Department of Mines.

Gold Mining in Ontario. Ontario Department of Mines.

PLANT OPERATIONS SERIES

Continuous Motion, Conveying, Stacking, Elevating, Etc. Brown Portable Conveying Machinery Co

Foamite Firefoam Extinguishing Apparatus at Work. Foamite Firefoam Co

MANUFACTURING CHEMISTS' ASSOCIATION

The report of the executive committee, Henry Howard, *chairman*, of the Manufacturing Chemists' Association for the year ending June 9, 1920, recounts the principal lines of work, "chiefly in connection with matters arising from the war and the termination of hostilities," which have occupied them.

The committee has coöperated largely with the Chemical Foundation, Inc. On their recommendation an advisory committee of the Foundation was formed, which has already brought about important advances in the work of the Foundation.

The Washington office, maintained jointly by the Manufacturing Chemists' Association, the National Fertilizer Association, and the Chemical Alliance, Inc., has kept closely in touch with legislation pertaining to chemical industry. In coöperation with the American Dyes Institute, the committee took an active part in urging the passage of the Longworth bill. They opposed the Tariff on Pyrites bill as highly injurious to the chemical industry of the country, and the bill will probably never be brought up for action.

The bill to increase salaries and personnel of the Patent Office received the active support of the committee until a rider was added, providing that the Federal Trade Commission may acquire patent rights and administer the same. This would allow intervention of the Government in industrial affairs to a dangerous degree. The Association, through membership in the National Industrial Conference Board, brought about organized opposition to the bill, with the result that its enactment was held up for the session.

In coöperation with the Chemical Alliance, Inc., and the National Fertilizer Association, an exceedingly comprehensive report embodying foreign trade statistics was drawn up and distributed to all members of the Association. The committee continues to keep in touch with foreign trade questions. They are maintaining the Association's membership in the National ForeignTrade Council, probably the leading foreign trade organization in the United States.

The Association was represented at an International Trade Conference held at Atlantic City in October 1919, under the auspices of the Chamber of Commerce of the United States. The one tangible result of the International Conference was the decision to create an International Chamber of Commerce. The organization meeting was called in Paris during the latter part of June. The Association was cordially invited to participate, and appointed as delegate Mr. C. Wilbur Miller, of the Davison Chemical Company.

As in previous years, the committee has taken up with the Bureau of Explosives many matters, among which are included standard tests for carboys, welded drums, carboy neck protectors, new type of carboy stopper, transportation of niter cake, transportation of hydrofluoric acid, and transportation of mixed acids.

CELLULOSE SYMPOSIUM FOR THE CHICAGO MEETING OF THE AMERICAN CHEMICAL SOCIETY

Under the able guidance of Mr. Jasper E. Crane, a Cellulose Symposium was organized as a part of the program of the Division of Industrial and Engineering Chemistry at the St. Louis meeting of the AMERICAN CHEMICAL SOCIETY last April. One of the objects of this symposium was to ascertain whether a Cellulose Section, if formed, would secure the interest and support of a sufficiently large number of chemists. The object of such a section would be to promote intercourse and coöperation between the chemists in the various cellulose industries. This group constitutes one of the largest and most important of American industries; all branches of it are intimately concerned in the problems of cellulose, and it seems highly desirable to promote technical activity in this country along these lines. The proposed section would serve as a clearing house for papers and information on cellulose technology, and should also play an important part in promoting research on the chemistry of cellulose.

The symposium at St. Louis was distinctly successful. The interest shown was so great that it was voted to hold a second Cellulose Symposium under the auspices of the Industrial Division at the Chicago meeting during the week of September 7. At this time, the advisability of forming a permanent Cellulose Section will be considered. An interesting program is being arranged, and a large attendance of those interested in cellulose is anticipated.

Arthur D. Little, Inc.
Cambridge, Mass.
July 6, 1920

G. J. Esselen, Jr.

TECHNICAL ASSOCIATION OF THE PULP AND PAPER INDUSTRY

On September 1 to 3, 1920, the fall meeting of the Technical Association of the Pulp and Paper Industry will be held at Saratoga Springs, N. Y., with headquarters at the Grand Union Hotel. The program gives assurance of a most interesting and instructive meeting.

Following the business session on Wednesday morning, September 1, at 9:30 o'clock, papers on special subjects will be presented, an especially important one being on the "Washing of Felts." In the evening members and guests will be entertained at dinner by the paper manufacturers of the Hudson River valley and vicinity.

Thursday, September 2, will be given up to mill visitations, followed by a steamboat excursion on Lake George in the evening. It has been arranged to pay visits of inspection by automobile to the plants of the International Paper Company, Finch, Pruyn & Co., Union Bag and Paper Corporation, Standard Wall Paper Co., and Sandy Hill Iron and Brass Works.

On Friday a visit to the works of the General Electric Company at Schenectady will show in the making the machinery and electrical apparatus used in pulp and paper mills. The visitors will subsequently be the guests of the General Electric Company at luncheon. In the afternoon it is planned to visit the felt mills of F. C. Huyck & Sons and the Albany Felt Company.

New York, N. Y.

Thomas J. Keenan, *Secretary*

CALENDAR OF MEETINGS

American Ceramic Society—Summer Meeting, LaSalle Hotel, Chicago, Ill., August 16–18, 1920.

American Institute of Mining and Metallurgical Engineers—122nd Meeting, Lake Superior, August 20 to September 3, 1920.

Technical Association of Pulp and Paper Industry—Fall Meeting, Saratoga Springs, N. Y., September 1 to 3, 1920.

American Chemical Society—Sixtieth (Annual) Meeting, Congress Hotel, Chicago, Ill., September 7 to 10, 1920.

Sixth National Exposition of Chemical Industries—Grand Central Palace, New York, N. Y., September 20 to 25, 1920

American Electrochemical Society—Fall Meeting, Hotel Statler, Cleveland, Ohio, September 30 to October 2, 1920.

NOTES AND CORRESPONDENCE

UNCOVERING THE PLATINUM THEFT AT THE OLD HICKORY POWDER PLANT, JACKSONVILLE, TENNESSEE

Between 4:30 P.M., March 17, and 9:00 A.M., March 18, 1920, almost 2200 g. of platinum laboratory ware, mainly crucibles, crucible covers, and dishes, valued at nearly $11,000, were stolen from the chemistry building of the Bureau of Standards.

During the first week in April, information was received of the arrest in New York of two men, giving their names as Robert E. Carter and Joseph Fredericks, who were attempting to dispose of about 280 troy ounces of platinum sponge. Lots of 50 oz. and 10 oz. had been left at the offices of two concerns in New York who deal in platinum and the other noble metals. The remainder of the sponge was later found in two rubber hot-water bottles in a small grip checked at the hotel where the two men were registered.

Between December 28 and 29, 1919, Roessler and Hasslacher Chemical Co., of Perth Amboy, N. J., had lost pure iridium sponge, platinum sponge, platinum sheet, and alloys of platinum and iridium containing 10 and 15 per cent iridium, as well as a considerable amount of gold and silver. Carter and Fredericks were arrested and detained under $5000 bail, the charge being that the platinum in their possession was stolen from the Roessler and Hasslacher Company. Acting on the idea that the platinum in question might include that taken from the Bureau of Standards, the Department of Justice was asked to investigate the matter.

In the preliminary hearings, Carter stated that his connection with Fredericks was merely casual, and that he and an associate named H. H. Brooks had obtained the platinum by placer mining on an unregistered claim about 100 miles north of Parry Sound, Ontario. The platinum was brought into the country without declaration to the Customs.

Carter gave certain false references in Ontario, among them the name of the Maxwell House as a hotel in Parry Sound. It was known from statistics of the U. S. Geological Survey, subsequently confirmed by the Canadian Department of Mines, that the total annual production of placer platinum in Canada did not exceed 25 ounces, and, furthermore, that no placer mining of platinum was carried out in Ontario.

In an interview with the representatives of the Bureau of Investigation and the Bureau of Standards, Carter described how "Brooks" had removed the gold from the crude platinum and had converted the remainder to sponge by dissolving it in aqua regia followed simply by drying and direct ignition of the chloride solution. This was done on the scene of the mining operations with reagents and equipment brought from Trenton and Montreal for this purpose.

It was obvious that a chemical analysis of the sponge would clearly distinguish between platinum that had undergone even the simplest refining and the crude mixture of platinum, iron (10 to 15 per cent), osmiridium, and sandy matter which would result from platinum ore treated in the manner described. It seemed probable, furthermore, that an exact analysis might help to decide the real origin of the metal in the event that Carter's story should be completely overthrown. Most of the platinum stolen in Perth Amboy was alloyed with 10 to 15 per cent of iridium. It was estimated that the laboratory ware lost by the Bureau of Standards would contain an average of about 1 per cent iridium with lesser amounts of rhodium and probably some palladium and iron. It was obvious that either of these lots of metal might be somewhat changed in composition through conversion into sponge. It was also possible that the seized sponge represented several lots of stolen platinum. It was to be expected, therefore, that the results of the analysis would be of greater value in pointing the way in which the investigation was to be directed than as testimony in the argument of any particular case.

The whole of Carter's Canadian story was discredited without much difficulty. Since the weight of platinum in Carter's possession was very nearly that of the platinum itself which had been stolen from the Roessler and Hasslacher Co., considering that all of the platinum had been carefully refined out of the platinum-iridium alloys, and since no thefts of equal magnitude had been reported, Carter and Fredericks were held in the Tombs awaiting trial on this indictment. The U. S. Customs Service was prepared to bring action against Carter, in the event of his acquittal, on the ground of his own statement that the platinum had been brought into the country without declaration.

A suggestion was made by Mr. Schauwecker, of the U. S. Assay Office, that the platinum in question might have been taken from one of the government munitions plants, certain of which used thousands of ounces of platinum in the manufacture of sulfuric acid by the contact process. The platinum used in the plants built during the war was refined by the U. S. Assay Office and converted to chloride solution either by the Assay Office or by the company which operated the plant. The diluted chloride solution was used to impregnate granular magnesium sulfate. Owing to the fact that some of these plants were in the process of being salvaged, an undetected theft might have been perpetrated.

At the request of the Bureau of Standards an inventory was taken by the Bureaus of Ordnance in the War and Navy Departments of all the platinum in their possession, but this revealed no shortage. Owing, however, to the fact that most of the platinum held by the War Department plants was still in the contact mass, it was apparent that the actual amount of platinum on hand could not have been determined without a very extensive series of assays or a complete recovery of the platinum in the mass.

In the meantime, the analysis of the sample of Carter's platinum had been completed by the platinum laboratory of the Bureau of Standards, with the following results:

	Per cent
Total platinum metals	99.20
Loss on ignition in porcelain crucible over blast lamp (volatile matter)	0.67
	99.87

Analysis calculated on "non-volatile" basis, *i. e.*, 100 per cent metals:

	Per cent
Iridium	0.33
Rhodium	0.10
Iron	0.01
Platinum	99.56
	100.00

Gold, copper, and nickel were not detected. Spectroscopic examination revealed the presence of a trace of palladium, as well as small amounts of aluminum, titanium, and magnesium. Traces of calcium and strontium, and possibly of silicon, were found. The sponge was apparently homogeneous except for the presence of small lumps of a yellowish brown substance which, on ignition, yielded platinum sponge, and gave off chlorine fumes. The brown lumps of incompletely ignited ammonium chloroplatinate revealed the fact that the conversion of the yellow salt to platinum sponge had been carried out with inadequate facilities or in haste.

The main thing to be learned from the chemical analysis was that the platinum was of unusual purity. The low iridium content was very strong evidence that the platinum did not originate from the alloys taken from the Roessler and Hasslacher Co., or from the ware lost by the Bureau of Standards or any other chemical laboratory. It was known that nearly all the other platinum of commerce contained from 0.5 to 1.0 per cent of iridium, if not more.

Nearly all the crude platinum which came into the country during the war was handled and refined by the U. S. Assay Office. Platinum 99.9 per cent pure and better was turned out in large quantities for the Nitrate Division of the Ordnance Department. (Most of this was subsequently alloyed with 1 per cent of iridium.) It was learned that the 5,800 odd ounces of sponge prepared for use in sulfuric acid manufacture at the War Department powder plant at Nitro, W. Va., and the nearly 13,800 oz. for the plant at Jacksonville, Tenn., were also of high purity, except that some of the platinum for use at Nitro contained about 0.5 per cent palladium. In view of these facts it was difficult to banish the idea that Carter's platinum came from one or the other of these plants, especially in view of two clues which might otherwise have seemed irrelevant.

It was found that the "Maxwell House" was a well-known hotel in Nashville, which is about 15 miles from the powder plant at Jacksonville; and it was also learned that at the time of Carter's arrest he had in his possession a cake of soap bearing the stamp of the Ruffner Hotel at Charleston, W. Va., in the immediate vicinity of the plant at Nitro. The soap also bore the initials "H. H. B." cut into it with a pocket knife. The photographic files of employees at the Nitro plant were unfortunately not complete, and Carter could not be identified. A visit of the Bureau of Standards representative to the Jacksonville plant, however, met with sudden success. Carter was identified as one H. H. Brown, who had been employed as salvage foreman until his departure from the plant on March 27. While it seemed that Brown had had no possible means of access to the platinum stocks of the plant, the manner in which he had obtained the 280 oz. found in his possession was explained by the next important development, which followed within an hour upon Brown's identification. This was the receipt by the Nashville office of the Bureau of Investigation of two letters, written by a man in the Tombs prison in New York to his wife. The letters referred to Robert Carter's arrest, and spoke of "$20,000 worth of stuff" for which she should get $85 to $90 per ounce, and told her to communicate with H. R. Crone, at the Old Hickory Powder Plant. Crone's arrest followed immediately upon Brown's confession that the platinum in his possession was obtained from Crone, who had stolen it from the reserve stock of platinum at the plant. Up to the time of the present writing, Crone has denied any guilt in his handling of the platinum at the plant.

About the first of March, Crone, as chief chemist of the plant, was directed to convert the reserve stock of platinum chloride solution, representing almost 2,300 oz. of platinum, to sponge, and to transfer it in sealed aluminum cans to the custody of the accounting office, where it was placed in a safe inside of the vault. About 75 oz. of platinum were handled at a time and the work was completed between the middle and the last of April. The safe contained 88 of these sealed containers, each bearing a label indicating the weight of platinum (about 25 oz.) it contained. After Crone's arrest, the contents of these cans were examined, and only two were found to contain platinum. One of these was the first one placed in the vault, while the other represented a quantity of chloride solution which would only half fill one of the cans. The remaining 86 cans contained a mixture of mercury with ordinary moist dirt, the ratio between the two being carefully adjusted so as to fill the can completely and give the correct gross weight to the sealed can.

One of the interesting and amusing phases of the case is that Crone first proposed to use lead filings as a substitute, but this meant an amount of hard work entirely out of proportion to the expected gains, and the scheme was abandoned in favor of the use of mercury and dirt.

It is presumed that Crone's defense will be that Brown is shielding the real thief, who made the substitution in the vault. Brown disclaims any knowledge of the whereabouts of the platinum except that which was in his possession, which is the total amount that has been recovered to date. Crone and Brown had both worked in the Parry Sound, Ontario, region, and had agreed upon the mining story as the most plausible and easily supported account of the origin of the platinum. There was no evidence to indicate that Fredericks was implicated in the theft of the platinum or in the attempted disposal of it, except that he acted as a guide for Brown in New York.

It was learned that Brown's stop at Charleston, while on the way to New York, was in the nature of a visit and apparently had no connection with the stolen platinum or the government plant at Nitro.

DRAWINGS OF STANDARD APPARATUS

Editor of the Journal of Industrial and Engineering Chemistry:

The work of the American Chemical Society Committee on Guaranteed Reagents and Standard Apparatus will necessarily be slow in regard to reagents and apparatus which have been in use many years. There is, however, one line of work on which immediate results may be obtained if the editors of journals and authors of papers will coöperate with the committee.

When a new piece of apparatus is described the committee would be glad to recommend as standard the exact form used by the author who describes it. The makers of apparatus would be glad to furnish their customers with apparatus like that of the author. One who has not given special attention to this point would be surprised to learn the small proportion of instances in which this is possible from the illustrations and descriptions published. In many cases there may be a wide range of dimensions which will prove entirely satisfactory. If the author considers this point he will know that any chemist who may desire to use the apparatus will know the proper dimensions, but makers who never have used such apparatus will be called upon to make it merely from the published drawing, and even if they all succeed in making something which can be used there may be several sizes and shapes made for the same piece of apparatus. This causes unnecessary work for makers and frequently dissatisfaction on the part of their customers.

A simple and obvious remedy would be for editors of journals to refuse to publish descriptions or illustrations of apparatus which were not sufficiently complete to enable any good workman to reproduce the article described. Editors to whom this suggestion has been made have expressed sympathy with the idea but have not been sure that they could enforce such a rule. Some authors are not skilled draftsmen and cannot easily have such work done for them.

The Association of Scientific Apparatus Makers of the United States of America is so interested in this question that when the matter was taken up with the chairman of its Committee on Standardization he agreed to take care of the drafting needed to make proper drawings of apparatus recommended as standard by the Committee on Guaranteed Reagents and Standard Apparatus of the American Chemical Society. Of course this offer should not be taken to cover the making of illustrations of every sort. It is intended primarily to take care of the newly described apparatus which the two committees consider likely to be used rather widely. If you will secure from authors complete dimensions, even on a rather rough drawing, the Association of Apparatus Makers will see to it that you have a suitable drawing for reproduction, provided the two committees think it worth while.

Authors who submit complete drawings and specifications will save some time in publication of papers if you adopt this policy. Any delay in publication of their papers on this account will cost much less to the interested parties than the present common practice of publishing with nothing to indicate the dimensions of apparatus described.

U. S. Geological Survey
Washington, D. C.
June 16, 1920

W. D. Collins, *Chairman,*
Committee on Guaranteed Reagents
and Standard Apparatus

JOSEPH A. HOLMES SAFETY ASSOCIATION

The Joseph A. Holmes Safety Association has recently announced the award of seven gold medals to miners for special deeds of bravery in the saving of human life in the United States during the last three years.

The Association was established in 1916 in memory of Dr. Joseph A Holmes, the creator and first director of the Bureau of Mines, and is composed of representatives of the leading technical and labor institutions of the United States, and receives its support through voluntary contributions.

In addition to the awards for heroism, the Association plans to recognize with awards the invention and application of safety devices in the industries concerned. It hopes in the future to devote attention to improvement of health conditions and to combating occupational diseases in mines and metallurgical establishments.

MACMICHAEL TORSIONAL VISCOSIMETER

Editor of the Journal of Industrial and Engineering Chemistry:

Referring to the article in the March issue of This Journal (page 282) on the MacMichael Torsional Viscosimeter, by Winslow H. Herschel, of the Bureau of Standards, I regret very much that I was not advised that this work was under consideration, as I would have been very glad to furnish one of the late model instruments for testing. The machine actually used was one of the very earliest models, not even provided with heating coils, or with a number of other improvements found in the later models.

Referring to the paper itself, my attention has been called to the fact that the term "poise" had been officially adopted as the name of the unit of viscosity in the C. G. S. system. I immediately wrote to the manufacturers requesting them to discontinue the use of the term "degrees M," equal to 0.1 poise, and to graduate all future machines for direct reading in poises, which I understand has been done.

It was never intended that this machine should be calibrated according to a mathematical formula, as this is obviously impossible, or at least impractical, from the very nature of the instrument.

The method recommended is to secure a sample of oil or other standard testing fluid, having a known viscosity nearly that of the samples to be tested. This sample should be tested by the Bureau of Standards at approximately the same temperature at which the machine is to be used, as 60°, 100°, or 210° F. With such a sample it is only the work of a moment to adjust the speed of the machine to give the reading on the dial corresponding to that of the standard sample. The readings for other fluids of the same general temperature and viscosity will be found closely accurate, the results, of course, being expressed directly in poises.

Where large differences in viscosity or temperature are dealt with, more than one standard testing sample is recommended, corresponding to various conditions to be met. It is also suggested that a large sample of fluid be procured, say, 0.5 or 1 gal., as there is always some slight loss in handling during tests. Of this, 100 cc. are to be sent to the Bureau of Standards for testing. The charge for this work is very moderate.

It is not particularly difficult to design a machine having a relatively simple mathematical treatment, giving primary readings for determining viscosity directly in poises. Such a machine would probably follow along the lines already laid down by Couette, using concentric cylinders, protecting end caps, etc. Such a machine, however, would probably not be well adapted to ordinary commercial uses.

The present machine was designed to fill a definite need in the testing of colloids and suspensions, as well as true solutions. It is not intended to give primary readings from which original data can be calculated, its function being to compare the viscosity of two fluids under similar conditions, the value of one of which is already known.

As furnished at present it will handle rapidly and easily tests from far below zero, in laboratories equipped for such work, up to 400° or 500° F. Also certain improvements are now being perfected by the manufacturers to extend the range of the instrument to viscosities much higher than could heretofore be measured, and to include means for testing the set of glue and similar materials.

The action of the machine depends on two laws, namely, that under similar circumstances:

(1) Deflection is proportional to speed.

(2) Deflection is proportional to viscosity.

When used as directed within the limits outlined above, these will be found to hold true with sufficient accuracy for a very wide range of practical purposes.

R. F. MacMichael

Consolidated Kansas City Smelting and Refining Co.
El Paso, Texas
April 12, 1920

. . . .

Editor of the Journal of Industrial and Engineering Chemistry:

In reply to the criticism of Mr. R. F. MacMichael, concerning my article in the March issue of This Journal, the following points may be offered:

As shown in Equation 10 there is not a constant ratio between poises and deflection, so that a machine graduated for direct reading in poises could not have a uniformly graduated scale. A more serious objection is that the graduation in poises must be based on the following assumptions if a single scale is used:

(1) That density is constant, or that the effects of its variation are negligible.

(2) That the variations of speed are negligible.

(3) That the clearance between the bottom of the disc and the bottom of the oil cup is not changed by removing and replacing the wire.

(4) That only one diameter of wire is used.

It is not believed that these assumptions are permissible, but that frequent recalibrations are necessary, and it is highly desirable purposely to vary the speed and the diameter of the wire in order to increase the range of measurable viscosity.

That the deflection is proportional to the speed and to the viscosity is, of course, true under certain conditions of speed, viscosity, and degree of accuracy required.

Winslow H. Herschel

Bureau of Standards
Washington, D. C.
May 27, 1920

THE EFFECT OF AIR IN STEAM ON THE COEFFICIENT OF HEAT TRANSMISSION—CORRECTION

In an article of the above title [This Journal, **12** (1920), 644] a printer's error was made in the final equation of that article, page 646. The equation as printed read:

$$\log_{10}h = 1 + 6.0240x$$

It should have read:

$$\log_{10}h = 1 + 0.0246x$$

C. S. Robinson

Cambridge, Mass.

WASHINGTON LETTER

By J. B. McDonnell, Union Trust Building, Washington, D. C.

INDUSTRIAL ALCOHOL SITUATION

Laboring under the excessively stringent regulations imposed under the prohibition enforcement act, which is administered by the Internal Revenue Bureau of the Treasury Department, the industrial alcohol industry found itself in an increasingly difficult situation. This was laid before Bureau officials at a conference held in June, attended by representatives of the alcohol, chemical, and drug industries, and by representatives of the War and Navy Departments.

Because of the illness of Commissioner Williams at the time, Paul Myers, assistant to the Commissioner, presided at the conference, at which several other Bureau officials were also present. The statements made were prepared in the form of a complete report for Mr. Williams. Improvement in his condition, however, has not occurred as rapidly as was expected and the whole question has not yet been passed upon by him. It was suggested that a special officer of the Bureau, having a technical knowledge sufficient to meet the situation, be appointed to undertake direct supervision of the enforcement of the law as applied to industrial alcohol. In this manner the industry would be relieved from hampering restrictions and red tape, now surrounding it as the result of its coming under the general enforcing squadron and many minor officials.

As a further aid the visitors suggested the appointment of an advisory board from the membership of the various organizations most closely interested.

Realization of the seriousness of the situation was expressed by Revenue officials, and there is little doubt that some action will be taken to relieve it. Just what this will be, of course, cannot be said at this time, inasmuch as Commissioner Williams, who will decide what is to be done, has not yet returned to his desk. Relief must and will be granted, other officials have stated, and it would not be surprising if the recommendation of the conference were adopted. Action is looked for within the next ten days or two weeks.

It was stated at the conference that, with a production capacity of 650,000 gal. of industrial alcohol, per day, the industry was producing only about 46 per cent of its capacity, and a serious shortage was threatened, with a curtailment in prospect.

With petroleum occupying such a prominent place on the industrial stage at present, it is not perhaps remarkable that some attention, whether wise or not, should have been turned to alcohol as a possible substitute for gasoline. Prior to adjournment of Congress, Representative Knutson, of Minnesota, introduced a resolution providing an appropriation for the Bureau of Chemistry of the Department of Agriculture to undertake a study to ascertain if alcohol could be turned to such a use. Later, Dr. Manning, until recently head of the Bureau of Mines of the Department of the Interior, questioned the good judgment of the Minnesota member in proposing to turn the investigation over to the Bureau of Chemistry. The Bureau of Mines should conduct the investigation and experiments, if made, Dr. Manning declared. The resolution, however, was lost in the shuffle among the many thousands that met a similar fate.

While there has not been any extensive investigation as a result of that resolution or a similar one, it apparently is the opinion of Government chemists here that alcohol is not destined to become a substitute for gasoline. It would be necessary to introduce other chemicals into it, and even then the price would be high, and doubt is expressed as to the possibility of turning it out in sufficient quantity. Its use would not be practicable, furthermore, without material changes being made in the motors built to consume gasoline.

BUREAU OF CHEMISTRY INVESTIGATIONS

Interesting developments with regard to the manufacture of dyestuffs from furfural, obtained from corn cobs, very probably will result from experiments which are being conducted by Dr. Johns, in charge of the color laboratory of the Bureau of Chemistry of the Department of Agriculture.

Experiments are now being conducted by the Bureau to ascertain the contents of the solutions resulting from washing of wool. Wool grease, it has been found, contains potash as well as nitrogenous substances. Samples of the liquids from wool washing establishments all over the country have been obtained by the Bureau, and analysis has definitely established the presence of these substances. Work is now progressing toward a method of extracting and separating them for commercial purposes.

LEGAL MATTERS

The suit instituted by Merck & Co. against the Alien Property Custodian for several thousands of dollars was dismissed by the court upon motion of the Government when the case came up for hearing here. It was shown that the company had not complied with all the legal technicalities required of it. Request by the company representatives that they be heard resulted in permission by the court to file a brief. This has not yet been filed.

Announcement was made the first of July by the Department of Justice of the commencement of a suit in equity, under the Sherman anti-trust act, against twelve of the principal manufacturers of linseed oil. The Government charges that the defendants had entered into an unlawful combination in October 1918 to enhance the price of their oil and to prevent lowering of prices. This was achieved by means of a so-called "Open Price Plan," the Department said. "The complaint shows that this 'Open Price Plan' includes the continuous interchange among the defendants of information as to their quotations, and as to the prices received by them in actual sales," the Department stated. "The Department of Justice has declared that the practice of keeping up prices by such 'plans' is not to be excused because the participants may have lodged information as to their 'plans' in the offices of governmental bureau or departments, or because of other like reasons. The Department of Justice has also stated that it will, if necessary, begin proceedings of an appropriate character to enforce the law against such practices." Reference is made to the "Open Competition Plan" of the American Hardwood Manufacturers' Association, which brought about prosecution and injunction against its use pending an appeal to the Supreme Court.

MISCELLANEOUS MATTERS

Investigation of public clinics established for the treatment and cure of drug addicts has been undertaken by the Government. Establishment of such clinics, it was announced recently, "hereafter will not have the indorsement of the Bureau of Internal Revenue." The Bureau is charged with administering the Harrison Anti-Narcotic Law, and its attitude was expressed in a letter sent out to all agents by Prohibition Commissioner Kramer, who said, "The net results obtained through the operation of such public clinics appear to have demonstrated conclusively that the cure of drug addiction through such means is a failure, and that hereafter no similar institution should have the endorsement of this Bureau."

The War Trade Board during the latter part of June sent out to consumers of dyestuffs its second questionnaire preparatory to issuing licenses for the importation of a six months' supply of such German dyestuffs as are needed. Consumers were warned by the Board that any requests for what appeared to be an undue amount would lead to delay, inasmuch as all such requests would be held up, pending complete and thorough investigation.

What action is to be taken in connection with German chemical reparation drugs apparently has not yet been decided by the Board. Although there has been some discussion of the subject, it has resulted for the most part in disagreement. It has been suggested that the Textile Alliance should handle these drugs, as it is handling the German dyestuffs. St. John Perret, however, is still in Europe, and War Trade Board officials here seem not to know when he expects to return.

Apparently the vacancies on the United States Tariff Commission have not yet been filled, in spite of the fact that the President gave recess appointments as members of the Commission to Prof. Marston T. Bogert, of Columbia University, and former Governor Samuel W. McCall, of Massachusetts. Both Professor Bogert and Governor McCall have signified their intention of declining the appointments at this time, but both would accept, it is understood, if assured that the appointments would be confirmed by the Senate. No salary attaches under a recess appointment unless such appointment is submitted later to the Senate and confirmed. Governor McCall was here a short time ago and conferred with Chairman Page of the Commission, and is understood to have explained during this visit that he did not feel free to accept the post under existing conditions. A similar attitude is believed to have been expressed by Dr. Bogert, who was hailed as one familiar with chemicals, at a time when such knowledge would be greatly needed in the work of the Commission.

July 16, 1920

LONDON LETTER

By Stephen Miall, 28, Belsize Grove, Hampstead, N. W. 3, England

It is a great honor to be invited to write some notes on matters of interest to chemists in the two great English speaking countries for the *Journal of Industrial and Engineering Chemistry*, and in this, my first contribution, I approach the subject with considerable diffidence. But I know, nevertheless, that on your side of the water you will be to my faults a little blind, and that both there and here we are confronted with similar problems and difficulties, and that a common effort will in the future, as in the past, enable us in time to solve them in a successful manner.

A PERIOD OF CHAOS

In applied chemistry we are faced in Great Britain with a state of uncertainty and chaos without parallel in the recollection of any of us. No one can form any just estimate of the future supply or price of coal or other fuels; no one has any sure data upon which to base an opinion as to the future of the principal metals and other raw materials. Accounts from Germany and Austria are singularly conflicting and it is not easy for us to know whether in chemical industry we are to export to those countries at a reasonable profit or whether we shall suffer from acute competition from those countries. And in our own financial state nothing seems certain beyond the fact that grievous and necessary taxation will continue for a long period and will hamper the development of business and the starting of new enterprises. We have recently lived through times infinitely more anxious, and our neighbors in France and Italy have far more difficult problems to solve than we have. Our anxieties are as nothing to theirs and the state of political industrial and financial chaos in Germany, Austria, and Russia is such as to be beyond conception. We are not merely perplexed by this; the aspect continually changes and it is hopeless for us to try and imagine what will happen in the east of Europe. In time some sort of settlement or stability will be achieved, but the details of the process are beyond the wit of man to imagine.

NITROGEN FIXATION

The general uncertainty, the enormous burden of taxation, the dearness of money and the unsettled state of labor, all contribute to restrict developments in chemical activity. Only one new enterprise of any magnitude is receiving attention here, and that is the erection at Billingham in the County of Durham of a considerable works for the fixation of atmospheric nitrogen by a modification of the Haber process. The company engaged in this work, Synthetic Ammonia and Nitrates, Ltd., is largely owned by Messrs. Brunner Mond and Co., Ltd., and the new works will have the coöperation of some of the leading manufacturers of explosives. As their consulting engineer and some others connected with the company have recently visited America, probably many of your readers are fairly familiar with the general nature of the proposition. In the works now being erected it is intended to manufacture upwards of one hundred tons of ammonia per day, and it is hoped that a large quantity of chloride of ammonia will be available as a fertilizer.

CHEMICAL SOCIETIES

In common with some other countries, we are here facing the problem of adjusting the needs of the various chemical societies to the new conditions under which we live. The cost of printing and paper has advanced rapidly and shows signs of yet further advancing. Chemistry is growing in bulk; the need for specializing is obvious and so the number of chemical societies steadily increases; the cost of managing each society also increases and the surplus income of each individual member is now so reduced by high prices and high taxation that he can ill spare the subscriptions necessary to maintain the usefulness of the various societies. There is a good deal of overlapping in the British chemical societies, and in a small country like ours a comparatively small number of chemists is called upon to take an active part in the management of several of these societies. "Many shall run to and fro and knowledge shall be increased," say the Scriptures, and assuredly there is much running to and fro in

London by men who, as a relaxation from their academic or industrial pursuits, attend meetings of the Chemical Society, the Society of Chemical Industry, the Society of Public Analysts, the Institute of Chemistry, *et hoc genus omne*. Sir William Pope, a past president of the Chemical Society and a future president of the Society of Chemical Industry, has for some time been advocating a coördination of chemical effort and a gathering of chemical societies, if not under one control, at any rate under one roof, whereby much money, energy, time, and temper may be saved. To do this will require a considerable effort. A sum of approximately a quarter of a million sterling will be necessary to provide a building suitable for the accommodation of the various chemical societies and a year or two of steady work will be involved. Contemporaneously an attempt will be made to tackle the awkward task of dealing with chemical literature and abstracts. In the course of the next month it is hoped to make a beginning of a campaign for collecting the necessary funds for these two purposes. This campaign will be directed by the Federal Council for Pure and Applied Chemistry which consists of nominees of all the important societies concerned in chemistry, Sir William Pope being the president.

The Society of Chemical Industry has received an invitation from the Canadian Section to hold the annual meeting in Montreal in the summer of 1921, and the council will recommend at the Society's meeting this July that the invitation be accepted. Many of us look forward with much pleasure to commencing or renewing our acquaintance with Canadian chemists on this occasion and we hope that we may also have an opportunity of meeting a goodly number of our American colleagues.

SHERINGHAM LIGHT

At the last meeting of the London Section of the Society of Chemical Industry there was an interesting exhibition of new plant and apparatus, the most important of which was perhaps the Sheringham light. This is intended to provide an artificial light as nearly similar to daylight as possible, so as to be suitable for the matching of colors, judging of colored materials, aniline dyes, pictures, etc. An incandescent lamp is fitted with a metallic hemisphere covering the lower half of the lamp and this reflects the bulk of the light upwards against a large reflector with a number of concentric rings colored yellow, green, and blue in proper proportions. By a judicious selection of the colors in the reflector a light is obtained whose spectrum is generally very similar to that of daylight, although the proportion of violet rays is less than that of daylight. The system of reflection absorbs something like half the incandescent light, but the invention shows great possibilities in connection with a perhaps rather limited number of purposes.

June 15, 1920

PARIS LETTER

By CHARLES LORMAND, 4, Avenue de l'Observatoire, Paris, France

It is with great pleasure that, at the request of Dr. Herty and with the advice of Mr. Gerard, secretary of the Société de Chimie Industrielle de France, I have undertaken the task of establishing a closer contact between American and French chemists by means of a monthly letter to your JOURNAL. It is an especially agreeable undertaking for me because it in a sense prolongs the mission to the United States which I filled during the war, when as a member of the French High Commission I was liaison officer between the Chemical Warfare Service and l'Inspection des Etudes Chimiques in France. When the armistice fortunately intervened and my military duty ceased, I had the good fortune to view the American chemical industry somewhat in detail, and also to visit several universities where are trained both research and industrial chemists, and the warm welcome which I always found on these occasions is pleasant to recollect. Some of the readers of THIS JOURNAL are therefore my friends, and it is with these auspicious ties of friendship that I open this correspondence.

It is not my task to provide a record of current scientific work—the articles published by the *Journal of Industrial and Engineering Chemistry* are sufficient for this. But I should like every month to keep you in touch with what is going on in France in the chemical world, as much from the purely scientific, as from the industrial viewpoint, and from the economic as well.

SCIENTIFIC RESEARCH IN FRANCE

Scientific research is at this moment passing through a serious crisis. It is going to lack personnel. The alarm has been sounded by Professor Daniel Berthelot, the son of Marcellin Berthelot. In a recent speech he called attention to the utilitarian direction of all scientific research, and more especially chemical. We have here in France many schools of chemistry, but they are all schools of industrial chemistry. Almost without exception they are concerned with producing the industrial chemist, and, little by little, we are seeing the laboratories attached to professorial chairs abandoned—laboratories such as that of Fremy at the Museum of Natural History, which have been the nurseries of the research chemists. The necessity which the younger generation feels of earning a living as soon as possible is the cause of this state of affairs. Add to this that most of the laboratories lack funds and cannot bear the cost of theoretical research whose economic profit may be far distant. The public authorities, however, seem willing to consider these questions, and to-day, for instance, you may see in the French parliament, a deputy, Mr. Maurice Barres, offer one of the arguments which you Americans have so wisely brought to the solution of the social problem:

> It is useless to quarrel with wealth; it is better to use its activity to create more; and in this creation of wealth we chemists have a large duty to fill.

FIXATION OF NITROGEN

In this connection I may call attention to what French chemists have done on the problem of the fixation of atmospheric nitrogen. France is primarily an agricultural nation. She has potash in Alsace, and phosphates in Tunisia; but she lacks nitric nitrogen, for which she must depend upon Chilean nitrate, and ammoniacal nitrogen, of which the supply is insufficient. After a long period of study, the problem has received a very promising solution. Mr. Georges Claude, to whom we already owe the investigation and manufacture of liquid air, has accomplished the fixation of atmospheric nitrogen as ammonia, using high pressures on a mixture of hydrogen and nitrogen. The semi-works plant which he has established at Montereau promises a speedy and successful solution. The ammonia will finally be converted to the carbonate; thence, with sodium chloride to ammonium chloride. An agricultural chemist, Georges Ville, has already demonstrated that ammonium chloride has a fertilizing action equal to any of the ammonium salts—sulfate or nitrate—now in use. On June 18 Mr. Claude is to give a conference on the results he has obtained, the details of which I shall later report to THIS JOURNAL. Your secretary, Dr. Parsons, is at present in France. The nitrogen problem is a familiar one to him, and he is extremely interested in the work of Mr. Claude.

We shall again see Dr. Parsons in Rome at the International Union of Pure and Applied Chemistry, where, with Mr. Chapin, he is representing the United States. There we shall tighten the bonds which should unite the chemists of our nations, allied in adversity and ready to labor together still in the employments of peace. Unification of analytical methods, organization of the Congress of Applied Chemistry, reorganization of the International Committee on Atomic Weights—such are some of the questions which will arise, and the importance of which is considerable.

It is by frequent contact that chemists will come to an understanding which will make for the general good. In my modest sphere I will do everything I can to maintain and strengthen this contact. From now on I place myself at the disposal of the readers of THIS JOURNAL for whatever they may need. When anyone needs information in a strange country he often does not know whom to ask. All the readers of the *Journal of Industrial and Engineering Chemistry* can send me requests for information. As the branches of chemistry are very numerous and my ability very slight, I cannot hope to give them the information, but will tell them at what door they should knock, whether they shall make their own requests or I take upon myself their transmission to the French chemist or manufacturer best qualified to reply.

Working together with the Bureau of the Société de Chimie Industrielle which will aid me in this task, I believe that I can interest American chemists, render them service, and show my appreciation of the cordiality which they have shown me.

June 19, 1920

INDUSTRIAL NOTES

According to the New York *Commercial*, an experimental garden for growing drugs is to be established at the Oregon Agricultural College with a view to encouraging the growing of drugs throughout Oregon. There are already large drug gardens in Washington and California, and it is believed that a profitable industry can be established.

At the annual meeting of the U. S. Potash Producers' Association, held in Chicago recently, the following officers were elected: President, W. E. Richardson, general manager of the Hord Co., Central City, Neb.; vice president and treasurer, A. C. Harragin, secretary of the American Trona Corporation, New York City; executive secretary, Frederick W. Brown, Washington, D. C. Records show that potash plants are operating full time and that several large plants are nearing completion. It is expected that the 1919 output will be doubled in 1920.

The U. S Civil Service Commission has recently announced an open competitive examination for assistant in assay laboratory. There is a vacancy in the office of the Director of the Mint, Treasury Department, Washington, D. C., at $1200 a year, and vacancies in positions requiring similar qualifications, at this or higher or lower salaries, will be filled from this examination, unless it is found in the interest of the service to fill any vacancy by reinstatement, transfer, or promotion. Competitors will be rated upon the sworn statements in their applications and upon corroborative evidence. Applications must be filed with the Civil Service Commission, Washington, D. C., by August 10, 1920.

The Commission also announces an examination for a metallurgical chemist at $6.88 a day and assistant metallurgical chemist at $5.12 a day. Vacancies at the U. S. Naval Ordnance Plant, South Charleston, W. Va. Competitors will not be required to report for examination, but will be rated on physical ability (10 points) and education and experience (90 points). Applications must be filed with the Civil Service Commission, Washington, D. C., by August 10, 1920.

The Commission announces open competitive examinations for assistant examiner, Patent Office, on August 4, 5, and 6; September 22, 23, and 24; November 3, 4, and 5, 1920. Vacancies in the Patent Office, Washington, D. C., at the entrance salary of $1,500 a year, with temporary increase, granted by Congress of $240 a year, to appointees who perform satisfactory service, and vacancies in positions requiring similar qualifications, at this or higher or lower salaries, will be filled from this examination unless it is found in the interest of the service to fill any vacancy by reinstatement, transfer, or promotion. Applicants should at once apply for Form 1312, stating the title of the examination desired, to the Civil Service Commission, Washington, D. C.

The Union Explosives Company has been incorporated with $250,000 capital at Clarksburg, W. Va.

About 100 men are at present engaged in reconstructing the plant formerly owned by the British Chemical Co., at Trenton, Ontario, and recently acquired by Chemical Products, Ltd., of Toronto. It is the company's intention to manufacture pharmaceutical products such as aspirin, phenacetin, salicylic acid, potassium permanganate, etc.,

An investigation of the potash deposits of Alsace has been made by H. S. Gale of the U. S. Geological Survey and F. K. Cameron of the Bureau of Mines, and the published report, containing illustrations and bibliography, may be obtained without charge from the Director of the Geological Survey, Washington, D. C.

Canada is now using about $5,000,000 worth of fertilizers a year. In 1918 the consumption was placed at $4,408,000. The value of imported fertilizers during last year was $1,200,233, of which $1,180,141 was from the United States. The value of fertilizers exported was $6,702,363, to which should be added $890,911 in the form of tankage, making a total of $7,592,274. Of this $5,670,667 went to the United States. In 1918 there were 15 establishments in Canada making commercial fertilizers exclusively, as against 12 in the same industry in the previous year. The beet sugar industry produces annually a large quantity of pulp, some of which is converted into cattle feed, and the remainder into fertilizer. Canadian coke plants produce thousands of tons of ammonium sulfate, most of which is used as a fertilizer. It is not largely used in Canada but constitutes an important export item, most of the Canadian ammonium sulfate going to the West Indies and the Southern United States for use on the sugar and cotton plantations.

A recent fire in plant No. 10 of the Chatfield Manufacturing Co., of Cincinnati, O., a coal-tar product concern, was extinguished by use of talcum powder. The fire spread rapidly and ignited a large tank of naphthalene and the firemen smothered the flames with talcum powder, which was dumped upon the fire in 50-pound sacks. The loss, estimated at $18,000, is covered by insurance. In the yard near the burning plant were huge tanks containing 300,000 gallons of oil. By the immediate and successful use of the talcum powder the flames were confined to one plant.

A large deposit of metallic arsenic is reported on Alder Island, one of the smaller islands of the Queen Charlotte group. Several claims have been staked covering the entire island, and samples taken indiscriminately give returns running from 18 per cent to 24 per cent arsenic, while the locator states it is possible to obtain specimens of the almost pure mineral. This is the first deposit of the kind on record in British Columbia, although for years arsenic has been produced as a by-product from the arsenopyrite ores of the Hedley Gold Mining Company.

The Southern Carbon Co., of Fairbanks, La., intends to establish three additional carbon black factories at Perryville, La., expending $1,000,000 on field developments.

The Spanish Ministry of Commerce has advised all Chambers of Commerce and industrial organizations in general to form a purchasing and distributing combination of all textile manufacturers needing German dyestuffs. The ministry wishes a Spanish syndicate to handle all the purchases of dyes in Germany and all Spanish manufacturers of textiles are officially warned against individually negotiating for dyes in Germany. This syndicate would apply to the Allied Commission at Coblenz for permission to export dyes from Germany.

In the report made to the House Committee on Interstate and Foreign Commerce, by Dr. Manning, former director of the Bureau of Mines, it is estimated that if gas containing as little as 0.35 per cent helium can be used, about 6,000,000 cu. ft. a week can be obtained. Although it is possible that new fields may be discovered, the gas resources of the United States and especially those of the helium-rich areas are fast declining and it is probable that in 20 years little or no gas will be produced in areas where 500,000 cu. ft. of helium are estimated to be wasted daily.

From 1910 to 1918 the importation of aniline dyes into the Argentine Republic was as follows:

	1910–14 Kilos	1915 Kilos	1916 Kilos	1917 Kilos	1918 Kilos
Germany	848,032	2,365	117	40	....
Belgium	29,554	541	...	....	....
United Kingdom	8,063	4,401	1,877	1,397	7,593
France	52,664	316	2,880	3,381	10,067
Italy	26,942	1,504	113	736	....
Switzerland	42,969	18,550	22,376	24,241	15,835
United States	3,961	7,513	27,292	97,109	247,257
Other Countries	6,372	2,181	10,258	5,795	3,676
TOTAL	1,018,557	37,371	64,913	132,699	284,428

An explosion, the cause of which has not been definitely determined, followed by a fire, occurred at the Burrage Works of the Atlantic Dyestuff Co., on June 12, resulting in the death of two of the company's employees and the destruction of a unit being devoted to the production of a special product. Repairs are being rapidly made to restore the plant to its normal capacity.

The Library of Congress has published a "List of References on Dyestuffs," compiled under the direction of H. H. B. Meyer, chief bibliographer. The list contains articles from periodicals as well as books on this general subject, and contains 1,650 items.

The Federal Trade Commission has cited the Star Provision Company, Malone Oil Company, and the Liberty Oil Products Company, all of Cleveland, Ohio, in a formal complaint of unfair competition in the oil and paint trade.

The Plant Protection Institute has just been organized with the advice and assistance of the National Research Council as a coöperative body of scientific experts on injurious insects and plant diseases and of manufacturers of insecticides, fungicides, and general chemicals, and apparatus used in fighting the enemies of field and orchard crops. The purpose of the Institute is to support and direct scientific research on methods of control of crop pests, and to further coöperation between scientific investigators and manufacturers of chemicals and appliances. It also expects to aid in the dissemination of scientifically correct information regarding the control of injurious insects and plant diseases

PERSONAL NOTES

Dr. Charles L. Parsons, secretary of the AMERICAN CHEMICAL SOCIETY, sailed from Liverpool on July 21, following the adjournment of the International Union of Pure and Applied Chemistry at Rome, where he acted as the American Representative.

Mr. C. R. Osland, formerly chemist and metallurgist of the Illinois Malleable Iron Co., Chicago, Ill., is at present employed in a similar capacity with the American Steel Foundries, E. St. Louis, Mo.

Mr. H. Berkson, formerly with the Corn Products Refining Co., is now connected with the Albers Bros. Milling Co., San Francisco, Cal., as chief chemist.

Mr. Albert T. Stearns is at present associated with the Nitrogen Corp., with main office in Providence, R. I.

Dr. James Brown, formerly research chemist for Zinsser and Co., Hastings-on-the-Hudson, has accepted a position as research chemist for the Calco Chemical Co., Bound Brook, N. J.

Dr. W. G. Crockett has resigned as professor of pharmacy in the College of Pharmacy of Baylor University, Dallas, Texas, to accept the position of professor of pharmacy in the department of pharmacy of the Medical College of Virginia, Richmond, Va.

Mr. Milton H. Fischer has severed his connections with the Sherwin-Williams Co., and is now in the chemical and steel brokerage business, trading under the name of the Midvale Products Corp., New York City.

Mr. R. P. Oilar, formerly official tester and grader of the New York Produce Exchange, has joined the Brecht Co., St. Louis, Mo., and will assume full charge of the oil refining department of that firm.

Mr. Charles W. Trigg, who has been engaged in research on coffee at the Mellon Institute for the past four years, has taken charge of the technical department of the King Coffee Products Corp., Detroit, Mich. Mr. Trigg will remain a senior fellow of the Institute.

Dr. Fred C. Blanck has resigned as food and drug commissioner of Maryland and associate in chemistry in the Johns Hopkins University to accept a position as director of inspection in the Del-Mar-Via Inspection District of the National Canners Association, with headquarters at Easton, Md.

Mr. Robert E. Kendall, formerly connected with E. I. du Pont de Nemours and Co., is now chemical superintendent of the Port Ivory, S. I., plant of Procter and Gamble Manufacturing Company.

Mr. E. P. Brewster, formerly assistant chemist for the Steel and Tube Company of America, Mayville, Wis., has accepted a similar position with Wickwire Bros., Cortland, N. Y.

Mr. Friend Lee Mickle has resigned as bacteriologist of the Bureau of Laboratories of the Connecticut State Department of Health and has been appointed director of laboratories for the Bureau of Health of Atlantic City, N. J.

Mr. Stroud Jordan is at present employed as chief chemist for Henry Heide, Inc., New York City. This work is largely research and chemical engineering along with a small amount of factory control.

Mr. Elton S. Boerstler, formerly with the B. F. Goodrich Company and the Firestone Tire and Rubber Co., at Akron, Ohio, has opened an office as consulting rubber engineer in Denver, Colo.

Mr. W. O. McMahon has left the real estate business in Birmingham, Ala., and has accepted the position of metallurgist for the Armiston Works of the Lynchburg Foundry Co., Lynchburg, Va.

Dr. Lauder W. Jones, dean of the School of Chemistry and also of the College of Engineering and Architecture of the University of Minnesota, has accepted an appointment as professor of organic chemistry at Princeton University, Princeton, N. J.

Dr. Edward Bartow, chief of the State Water Survey Division of Illinois for the past fifteen years and professor of sanitary chemistry at the University of Illinois, has been appointed the new head of the department of chemistry, University of Iowa, Iowa City, Ia., succeeding **Prof. E. W. Rockwood**, who is relieved of his administrative duties at his own request although retaining his full professorship in the department.

The honorary degree of Doctor of Science was recently conferred upon **Mr. Henry B. Faber** by Emory University, Atlanta, Ga.

Mr. A. J. Lewis resigned recently from the Bureau of Standards, Washington, D. C., where he was engaged in paint and varnish analysis as assistant chemist, and is at present located with the H. H. Franklin Manufacturing Co., Syracuse, N. Y., as research chemist in paints, varnishes, and enamels.

Mr. R. G. Upton, formerly with the Texas State Board of Health as assistant sanitary engineer, now has charge of both inspection and laboratory work for the City of Port Arthur, Texas, where he is chemist and sanitary engineer.

Mr. Charles S. Howard, formerly an instructor in the department of electrical engineering and physics at the U. S. Naval Academy, has accepted a position as junior chemist in the Quality of Water Division of the Water Resources Branch of the U. S. Geological Survey, Washington, D. C.

Mr. A. W. Gauger resigned the Harvard Fellowship in chemistry at Princeton University to join the staff of the research laboratory of the American Sheet and Tin Plate Co., Pittsburgh, Pa., as research associate.

Mr. Fred West, chief of the U. S. Customs Laboratory of the Port of New York, recently resigned that position to become chief chemist for the new factory of the United Drug Company at St. Louis, Mo.

Dr. R. L. Sebastian, formerly engaged in magnesite investigation with the U. S. Bureau of Mines, Berkeley Station, Cal., has accepted a position as research chemist with the Barrett Co., Frankford, Pa.

Mr. B. F. Dodge has left the chemical department of the du Pont Company where he was assistant manager of the inspection and standards division, and is as present with the Lewis Recovery Corp., of Boston, Mass., where he is working on the recovery of volatile solvents in the rubber industry.

Mr. Howard B. Bishop has resigned from the National Aniline and Chemical Co., and has opened an office as consulting chemist at 101 Park Avenue, New York, N. Y.

Mr. W. D. Collins has left the Bureau of Chemistry of the Department of Agriculture to take charge of work on quality of water for the U. S. Geological Survey.

Mr. R. B. Moore, chief chemist of the Bureau of Mines, and **Mr. Dorsey Lyon**, supervisor of mining experiment stations, are going South to inspect sites suggested for a mining experiment station to deal with problems of non-metallic mining, as provided for at the last session of Congress.

The honorary degree of doctor of laws has been conferred upon **Dr. Simon Flexner**, director of the Laboratories of the Rockefeller Institute for Medical Research, by Cambridge University.

Mr. E. C. Boudreaux has severed his connection with the Bogalusa Paper Co., Bogalusa, La., and has taken a position with Penick and Ford, Ltd., Inc., of New Orleans, La.

Prof. Arthur M. Pardee has resigned from the chair of chemistry at Washington and Jefferson College, Washington, Pa., to become the head of the department and professor of chemistry at the University of South Dakota, Vermillion, S. D.

Mr. Paul M. Giesy has left his former position as research chemist, dyestuff research department, Grasselli Chemical Co., to accept a position with the Calco Chemical Co., where he is in charge of the beta-naphthol control laboratory. Mr. Giesy received the degree of Ph.D. from Columbia University in June.

Mr. Sidney R. Dodd, formerly plant research chemist, in charge of the laboratory for the Radium Luminous Materials Corp., Orange, N. J., is at present with the Vulcanized Rubber Co., at its factory in Morrisville, Pa., where he is organizing a laboratory of which he will be in charge when it is completed.

Mr. Arthur C. Metcalf has resigned as junior chemist, Bureau of Chemistry, U. S. Department of Agriculture, to become chemist for the Republic Packing Corp., Lockport, N. Y.

Mr. Ferdinand A. Collatz has resigned his assistantship in the department of biochemistry, University of Minnesota, to accept a research fellowship with the American Institute of Baking, Minneapolis, Minn.

Dr. Louis J. Gillespie, professor of physical chemistry at Syracuse University, who was formerly with the Department of Agriculture, Washington, D. C., has resigned to go to the Massachusetts Institute of Technology as assistant professor of physicochemical research in the research laboratories of physical chemistry.

GOVERNMENT PUBLICATIONS

By Nellie A. Parkinson, Bureau of Chemistry, Washington, D. C.

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

CONGRESSIONAL COMMITTEES

Wood Pulp. Exportation of pulp wood from Canada to the United States, hearings on S. J. Res. 152, authorizing the appointment of a commission to confer with Dominion government or provincial governments of Quebec, Ontario, and New Brunswick as to certain restrictive orders in council of said provinces relative to the exportation of pulp wood therefrom to the United States. March 9 to April 27, 1920. 176 pp.

Wood Pulp. Report to accompany S. J. Res. 152; submitted by Mr Porter. House Report 1039. 2 pp. May 26, 1920.

Paper. Newsprint paper industry, hearing before subcommittee pursuant to S. Res. 164, authorizing the Committee on Manufactures to investigate newsprint paper industry. Parts I–V. 518 pp. 1920.

STATE DEPARTMENT

Petroleum. Restrictions on American petroleum prospectors in certain foreign countries, in response to resolution, report, with accompanying enclosures, in regard to restrictions imposed by certain foreign countries upon citizens of the United States in prospecting for or acquiring lands containing petroleum within territory under the jurisdiction and influence of such countries. Senate Document 272. 17 pp. May 17, 1920.

TREASURY DEPARTMENT

Denatured Alcohol. Regulations and instructions relating to manufacture, sale, and use of denatured alcohol under the act of June 7, 1906, amendatory act of March 2, 1907, and act of October 3, 1913. Regulation 30 revised. 72 pp. Paper, 10 cents. Reprint, 1920.

UNITED STATES PUBLIC HEALTH SERVICE

The Regulation of Biological Products in England. 35, 1400. The Minister of Health of England has recently appointed a committee to consider and advise upon legislative and administrative measures to be taken for the effective control of the quality and authenticity of such therapeutic substances offered for sale as can be tested adequately by direct chemical means.

Delay in Shipment of Materials Used in the Purification of Water Supplies. 35, 1536–7. Difficulties in transportation have prevented prompt shipment of chlorine, hypochlorite, bauxite, alum, soda ash, copperas, lime, and other materials used in water purification. This has resulted in a very serious menace to life and health, and some epidemics are reported to have been occasioned thereby.

Adsorption of Cyanide Gas by Foodstuffs. 35, 1597. The conclusion drawn from the experiments conducted is that the possibility of food poisoning occurring from food materials exposed to cyanide gas is extremely remote.

GEOLOGICAL SURVEY

Cobalt, Molybdenum, Tantalum, Titanium, Radium, Uranium, and Vanadium in 1918. F. L. Hess. Separate from Mineral Resources of the United States, 1918. Part I. 27 pp. Published June 29, 1920.

Nickel in 1918. F. L. Hess. Separate from Mineral Resources of the United States, 1918, Part I. 8 pp. Published June 29, 1920. The only nickel produced in the United States in 1918 was about 440 short tons, saved as a by-product in the electrolytic refining of copper. As heretofore, the country obtained its supply from Canada and, in much smaller quantity, from New Caledonian ores matted in France.

BUREAU OF MINES

Monthly Statement of Coal Mine Fatalities in the United States, March 1920. W. W. Adams. 8 pp. Paper, 5 cents. May 1920.

Comparative Fuel Values of Gasoline and Denatured Alcohol in Internal Combustion Engines. Bulletin 43. Paper, 20 cents. Issued June 1920. Covers gasoline and denatured alcohol as engine fuels, apparatus used in tests, procedure of tests and deductions from tests.

Extinguishing and Preventing Oil and Gas Fires. C. P. Bowie. Bulletin 170; Petroleum Technology 48. 56 pp. Paper, 20 cents. Revised Edition, 1920. Contains a bibliography on oil fire hazards and prevention, and lists of Bureau of Mines publications on petroleum technology.

Mining and Preparing Domestic Graphite for Crucible Use. G. D. Dub and F. G. Moses. **With a Chapter on Methods of Analysis Used by the Bureau of Mines.** G. B. Taylor and W. A. Selvig. Bulletin 112. 80 pp. Paper, 20 cents. The bulletin is in two parts. The first part describes the methods of mining and milling used, suggests a standard method of sampling finished graphite, and describes a rapid and convenient method of analysis developed at the Pittsburgh Station of the Bureau of Mines, to which had been assigned the analytical and microscopic work. The second part describes experiments on the concentration and milling of graphite which were made at the Salt Lake City, Utah, station.

Manganese: Uses, Preparations, Mining Costs and Production of Ferro-alloys. C. M. Weld, and others. Bulletin 173. 209 pp. Paper, 30 cents. 1920. Includes a selected bibliography on manganese deposits and a list of Bureau of Mines publications on metallurgy.

BUREAU OF STANDARDS

Recommended Specifications for Quicklime and Hydrated Lime for Use in the Cooking of Rags for the Manufacture of Paper. Circular 96. 5 pp. Paper, 5 cents. Issued June 15, 1920. This is the first of a series of specifications for the lime used in various chemical industries, and covers the use of lime in cooking rags, the definitions of quicklime and hydrated lime, and the general requirements and methods of sampling and testing.

The Double Polarization Method for Estimation of Sucrose, and the Evaluation of the Clerget Divisor. R. F. Jackson and C. L. Gillis. Scientific Paper 375. 70 pp. Paper, 10 cents. Issued March 30, 1920. The velocity of inversion of sucrose was measured at temperatures from 20° to 90° C. and was found to follow the exponential law first proposed by Arrhenius. Rates of reaction were measured for three different concentrations of hydrochloric acid. The time required under different conditions to produce 99.99 per cent inversion was computed and tabulated. The rate of decomposition of invert sugar in the presence of hydrochloric acid at different temperatures was measured and the conclusion drawn that for the Clerget analysis 60° C. is the most satisfactory temperature. The basic value of the Clerget divisor was found to be 143.25

instead of 142.66. The presence of hydrochloric acid increases the levo rotation of invert sugar. It was found that the effect of hydrochloric acid could be duplicated by neutral salts. It is proposed to add 2.315 g. of NaCl to the solution for direct polarization to secure a constant rotation of invert sugar when it exists as an impurity. The effect of these reagents on the rotation of sucrose was measured. Four methods of analytical procedure were suggested and sucrose solutions of known composition analyzed by them. The analytical results were found to be accurate.

Intercrystalline Brittleness of Lead. H. S. Rawdon. Scientific Paper 377. 18 pp. Paper, 5 cents. Issued April 6, 1920.

Porosity and Volume Changes of Clay Fire Bricks at Furnace Temperatures. G. A. Loomis. Technologic Paper 159. 29 pp. Paper, 5 cents. Issued April 26, 1920.

Effects of Oils, Greases, and Degree of Tannage on the Physical Properties of Russet Harness Leather. R. C. Bowker and J. B. Churchill, Director, American Leather Research Laboratory. Technologic Paper 160. 18 pp. Paper, 5 cents. Issued April 17, 1920. The following general conclusions were drawn:

1—That the amount of stuffing content affects the tensile strength of the leather and that there is a point beyond which the amount of stuffing content used does not add to the strength and may actually serve to decrease it.

2—That the tensile strength is greater for leather tanned a short time than for leather given a long-time tannage, and that the degree of tannage also affects the firmness of the leather, the longer-time tannage producing leather more resistant to shear when used with a buckle.

3—That the use of a mixture of 50 per cent Breton mineral oil and 50 per cent tallow in stuffing the hide does not affect the physical properties of new leather in a manner different than that caused by the use of cod oil.

A Pycnometer for the Determination of Density of Molasses. Technologic Paper 161. W. B. Newkirk. 7 pp. Paper, 5 cents. Issued April 6, 1920. A new pycnometer design has been developed which permits greater accuracy in density determinations of molasses than has been possible heretofore.

Extraction of Rubber Goods. S. W. Epstein and B. L. Gonyo. Technologic Paper 162. 13 pp. Paper, 5 cents. Issued April 9, 1920. It was found that extraction for 8 hrs. with acetone, followed by 4 hrs. extraction with chloroform, does not remove all soluble material from some rubber compounds. After a rubber sample has been extracted with acetone it was found: (*a*) That chloroform in every case extracted slightly more material than carbon bisulfide; and (*b*) that constant boiling mixtures extracted from many cheap compounds considerably more material than either chloroform or carbon bisulfide. The constant boiling mixture of 68 per cent chloroform and 32 per cent acetone exhibits a marked ability to dissolve vulcanized rubber, as contrasted with the mixture of 55 per cent carbon bisulfide and 45 per cent acetone, which exhibits this ability hardly at all.

A constant boiling mixture 55 per cent carbon bisulfide and 45 per cent acetone used in place of acetone and chloroform to extract rubber samples is preferable, in that:

(*a*) It eliminates one extraction with the necessary weighings.

(*b*) Extraction is complete in 8 hrs., while the acetone and chloroform extractions require a total of 12 hrs.

(*c*) The extraction of free sulfur is complete.

(*d*) A rubber analysis in which the mixed solvent is used is more accurate than that in which acetone and chloroform are used separately, because: (1) Little or no rubber is dissolved by this mixture, as compared with chloroform, which will in some cases dissolve considerable quantities; (2) the extraction of cheap rubber compounds is more complete, since the extracts obtained are greater than the sum of the acetone and chloroform extracts.

DEPARTMENT OF AGRICULTURE

TNT as a Blasting Explosive. C. E. Munroe and S. P. Howell. Department Circular 94. 24 pp. Paper, 10 cents. May 1920.

The Flow of Water in Dredged Drainage Ditches. C. E. Ramser. Department Bulletin 832. 60 pp. Paper, 30 cents. Issued June 7, 1920.

Examination of Frozen Egg Products and Interpretation of Results. H. W. Redfield. Department Bulletin 846. 96 pp. June 5, 1920. Paper, 10 cents.

Articles from the Journal of Agricultural Research

Effect of Drugs on Milk and Fat Production. F. A. Hays and M. G. Thomas. 19 (May 1, 1920), 123–30.

Influence of Fermentation on the Starch Content of Experimental Silage. A. W. Dox and Lester Yoder. 19 (May 15, 1920), 173–9.

Effect of Premature Freezing on Composition of Wheat. M. J. Blish. 19 (May 15, 1920), 181–8.

Effect of Manure-Sulfur Composts upon the Availability of the Potassium of Greensand. A. G. McCall. 19 (June 15, 1920), 239–56.

COMMERCE REPORTS—JUNE 1920

The use of grasses, reeds, and rushes of tropical Africa is suggested for **paper making**. (P. 1235)

The final report of the British Nitrogen Products Committee recommended the framing of a coördinated policy for safeguarding the **future nitrogen requirements** of the Empire and urged that this should be done by an Imperial authority. Attention was called to the saltpeter earths and water-power possibilities of India and the conclusion was reached that India, with its varied climatic conditions and soil and its variety of crop production, must in time give an outlet for very large quantities of all classes of artificial fertilizers. (Pp. 1247–9)

Montreal and New York interests are said to be identified with the new $2,500,000 **pulp** and **paper mill** enterprise of Quebec Province. (P. 1249)

The 18 furnaces in the Belgian **window-glass** industry are turning out monthly 1,800,000 to 2,000,000 sq. ft. of glass. Nine-tenths of this production is exported and yet Belgium is unable to fill numerous orders which are being received from all over the world. (P. 1251)

Annual reports of the **artificial silk** companies in Belgium indicate the prosperity in this industry. (P. 1251)

While the **vegetable** and **essential oil** trade of Hongkong shows considerable expansion, there was not the increase in the exports of essential, and especially other vegetable oils, out of Hongkong in 1919 that was anticipated. (P. 1252)

There are three **ammoniacal** and **caustic soda** factories in Poland which will suffice for that country's needs. In one of these factories caustic soda is made by an electrolytic process. (P. 1262)

The British-Australasian Lead Manufacturers' Proprietary, Ltd., is erecting extensive works in Australia for the production of **white lead**. The company also purposes giving attention to the manufacture of prepared paints, dry colors, varnishes, and, in fact, to the whole requirements of the oil and color trade except the crushing of linseed. (P. 1271)

The Swedish **wood-pulp** trade in 1919 is reviewed. The following table shows the total output of sulfite cellulose during the last seven years as compared with the normal annual capacity of the mills:

Years	Production Metric Tons	Normal capacity (Approximate) Metric Tons	Production in Per cent of Capacity Per cent
1913	699,937	700,000	100
1914	714,747	750,000	95
1915	742,000	760,000	97
1916	771,302	790,000	98
1917	554,966	825,000	67
1918	476,307	850,000	56
1919	581,167	850,000	69

The production of sulfate cellulose during the years 1915–1919, compared with the normal productive capacity of the mills, was as follows:

Years	Production Metric Tons	Normal Capacity Metric Tons	Production in Per cent of Capacity Per cent
1915	179,240	190,000	91
1916	217,102	218,000	100
1917	209,439	230,000	90
1918	181,917	235,000	77.5
1919	103,297	246,000	42

(Pp. 1282–5)

A steadily growing demand for **foreign paints, varnishes, lead,** and **colors** is reported from the Tientsin consular district of China. (P. 1286)

The patent fuel works of Wales require for the manufacture of their briquets or ovoids great quantities of **tar** and **pitch**, which must be imported as they are not produced in Great Britain. (P. 1287)

There is a great demand for **soap** in the Mukden Consular District. The demand for laundry soap exceeds that for toilet soap. (P. 1342–4)

The **kerosene** trade of South China has assumed its pre-war characteristics and volume and in value has reached far greater proportions than ever before. (P. 1347)

The **oilseed** industry of Southern Rhodesia is reviewed. The peanut is the most important oil-yielding product, sunflower seed and linseed ranking next in importance. The latter is grown only for home use at the present time. (P. 1358)

An **oil pipe line** is proposed from Drohobyez to Danzig, 1000 kilometers in length, which would have as an object the pumping of petroleum directly from its sources to the Polish littoral, and its exportation thence in foreign bottoms, supplying on its way the different Polish towns. (P. 1383)

The Polish **paper** industry requires not only machinery but also felt, brass rivets, and American resin. (Pp. 1404–6)

The details of the new British combine for the mass production of table **glassware** have now been made public. (P. 1421)

A cutlery research association has been organized for Sheffield, known as the British Cutlery Research Association. Forty firms have already promised their support, amounting to a minimum annual income of $7,500, and for the encouragement of the movement the government has set aside £1,000,000. (Pp. 1422–3)

Out of a total exportation of 1,899 metric tons of **licorice root** from Italy in 1919, 1,304 metric tons were shipped to the United States. (P. 1423)

Linseed oil, linseed, and other raw materials are being concentrated for export from Siberia by the northern route. (P. 1425)

There are signs that the **china-clay** export trade of England is beginning to revive after the severe blow dealt it by the war and by the exchange and transport difficulties that have hindered its development since the armistice. (Pp. 1436–7)

The **mining industry** in Abyssinia is undeveloped. There are reported evidences of commercial deposits of coal, iron, oil, sulfur, gold, silver, copper, and potash, but none of these deposits, except potash, are now being worked on a commercial scale. It is planned, however, soon to undertake the exploitation of Abyssinian mineral resources. (Pp. 1438–9)

The Indian **chemical** industry is in need of up-to-date chemical engineering plants and appliances. Indian chemists are now at work on the following problems, among others: Colloidal medicinal preparations, the preparation of suitable chromate from chrome iron without the use of caustic soda or sodium carbonate, the purification of various local oils, the manufacture of acetone, the production of caustic soda, ammonia, and the various ammonium salts, and the production of sulfuric acid on a large scale. Refined petroleum, many of the belladonna preparations, tannic and gallic acids, salicylic acid and its salts, and a number of the coal-tar derivatives are being made in India. New chemical industries are to be established for the utilization of the alkali deposits. Potash production is a fairly old established industry. Very little has been done in connection with the distillation of wood for charcoal, wood naphtha, wood tar, and acetate of lime. (Pp. 1440–1)

The situation of the **dye trade** in Hongkong at the present time is decidedly uncertain. In the past two years the United States has built up a considerable trade in aniline and artificial indigo. In December 1919 the Hongkong government prohibited the import of any artificial dyes not of British manufacture. This order was later modified to permit the import of American or other non-British dyes for reëxport, but the regulations are so onerous that Hongkong importers have hesitated to order American dyes except for transshipment and the British dye manufacturers have not responded to the demands of the market. (Pp. 1447–9)

A grave shortage of **print paper** is reported in the United Kingdom. (P. 1458)

Finland offers a very good market for chemicals used in the **cellulose, paper, textile,** and **tanning industries.** (P. 1464)

Swedish **newsprint** and **wood-pulp** production is reviewed. Swedish operators are receiving $348 a ton for their product, as against $187 in November 1919. (Pp. 1473–8)

China is getting practically all of her **copper** from Japan. But Japan has not succeeded in producing copper at as low a cost as the United States, as is indicated by the fact that Japan has been buying and importing copper from the United States, some of which has been passed on to China. Chinese demands for copper are certain to grow and a market for the American product is therefore suggested. (Pp. 1479–81)

Philippine **asbestos** is reported to be available for export. (P. 1484)

American **dyes** imported into Burma are reported so satisfactory that importers have signified their desire to receive more, especially of those adapted to dyeing silks. (Pp. 1484–5)

The **lac** industry of India is reviewed. (Pp. 1488–92)

The feeling in the **nitrate** industry in Chile at the present time is most optimistic, based on the probable demands from Central Europe, principally Germany, which has always been a large user of nitrate as fertilizer, and the fact that the production of the electrically manufactured nitrate has not been so successful as anticipated, and cannot compete with the natural product of the deposits in Chile, either in quality or price. (P. 1498)

In addition to the oil fields, Rumania is rich in minerals, the chief ones being **salt, coal,** and **ores.** (P. 1510–11)

The trade in **glass** and **glassware** in Hongkong has developed rather lively competition in the past few months, and there is considerable doubt as to what proportion of it the United States will retain on a permanent basis. Undoubtedly, there is a good field for American glassware, if it is fairly cultivated. (Pp. 1526–7)

A **starch** and **glucose** factory is being constructed on a very large scale in South Africa. (P. 1527)

The **vegetable-oil-bearing** products and vegetable-oil industry in French and British West Africa are reviewed. (Pp. 1534–8)

Hongkong's trade in **peanuts** and **oil** is reviewed. (Pp. 1539–41)

The consumption of **paint** and **varnish** in Sicily is relatively heavy. Stocks from the United States have never been offered but there is no doubt American products would sell were they available. (P. 1542)

There is a strong demand for **paraffin wax** in Sicily, especially in Palermo. (P. 1542)

In view of the present depressed market conditions, the Southern India Skin and Hide Merchants' Association resolved that the **tanning** of skins and shipments of tanned skins to all destinations be temporarily stopped. (P. 1551)

It is reported that the States of Para, Maranhao, and Ceara, Brazil, possess many minerals in paying quantities, among which are **gold, manganese, bauxite, copper,** and **platinum.** (P. 1563)

A good market is reported for **paints, oils,** and **varnishes** in South Manchuria. (P. 1599)

Substantial and relatively satisfactory progress was reported at the annual general meeting of the British **Dyestuffs** Corporation. While foreign supplies may be necessary for a time, it was the consensus of opinion that such supplies should be imported only under some system that will guarantee that the danger of complete or partial foreign monopoly will not reappear. (P. 1602)

Forty **paper mills** in Japan are to close because it is claimed that the slump in this industry since the war has wiped out nearly all of the $500,000,000 profit made during the last five years. (P. 1606)

Japanese importers are trying to dispose of surplus stocks of **sulfate of ammonia** by taking advantage of the requirements of the Java market for this fertilizer for the sugar-cane crop. (P. 1606)

The output of potash in Alsace for 1920 is estimated at 1,320,000 metric tons of crude potash. In view of impending developments the output for 1921 is estimated at 2,040,000 metric tons and for 1922 at 2,340,000 metric tons of crude potash. (P. 1611)

The opinion is current in Sweden that American **tin plate** lacks the finish of the English, but is softer. Manufacturers of tins for the anchovies industry prefer the American tin plate on account of its flexibility. Sheet-iron workers, on the other hand, prefer the English variety. (P. 1613)

The mining of the rare mineral **osmiridium** in Tasmania is attracting widespread attention at present, and it is said that the island promises to be the world's chief producer for some time to come. (P. 1615)

A very deep interest in the subject of the regulation of sales of British-made **narcotics,** more especially morphine and its derivatives, to foreign countries seems to be taken in responsible official circles in Great Britain. (P. 1627)

During the war the scarcity of paper pulp in the Spanish market caused Spanish paper makers to consider the use of **esparto.** While esparto has exceptional qualities for certain uses in **paper making,** its fibers are not such as will allow its substitution for all the purposes for which wood pulp is used. It is not suited for the manufacture of wrapping paper. It can, however, be used in larger proportions than has heretofore been the practice in most other grades. (Pp. 1633–5)

The estimated supply of **sumac** on hand in Sicily is 10,000 tons. There are 1000 tons available for immediate export. (P. 1649)

Conditions in the British **iron and steel** trade are approaching normal as far as production and merchandising are concerned and the industry is rapidly approaching a sound and healthy expansion. The following table shows the production of iron and steel in Great Britain from 1913 to April 1, 1920:

Period	Pig Iron Tons	Steel Ingots and Castings Tons
1913 total	10,260,000	7,664,000
Monthly average for 1913	855,000	639,000
1918 total	9,072,000	9,591,000
Monthly average for 1918	756,000	799,000
1919 total	7,398,000	7,894,000
Monthly average for 1919	617,000	658,000
January 1920, total	665,000	754,000
February 1920, total	645,000	798,000
March 1920, total	699,000	840,000

(Pp. 1655–9)

Notwithstanding constantly increasing production, Czecho-Slovak **glass factories** are oversold for some time to come. New companies have been organized with large modern plants and it is expected that the normal pre-war capacity will be increased by 50 per cent. (Pp. 1667–9)

The **salt industry** of Poland has before it unlimited possibilities, because the supply is nearly inexhaustible. Poland hopes in the near future to compete in the salt industry of the world. (Pp. 1670–1)

The sharp decline since the high prices of 1916 in the average prices of Japanese phosphorus is indicated below.

Period	Average Price per 100 lbs Yellow	Average Price per 100 lbs Red
Just prior to the war	$33.12	$48.65
Two months after outbreak of war	89.73	134.60
June 1916	199.40	249.25
April 1920	48.85	47.36

(P. 1691)

A French decree of June 16, 1920, prohibits from the date of publication (June 19) the importation into France and Algeria of all **newsprint paper** and wood pulp for the manufacture of newsprint paper. (P. 1697)

The total amount of dyes and **dyestuffs** exported from the United States during the calendar year 1919 was $17,084,435. Japan ranked first among the principal countries of destination, with imports valued at $3,196,550, and Canada second, with $2,143,097 worth. Other important markets were China, British India, England, Brazil, and France. (P. 1699)

The War Trade Board Section of the War Department is now prepared to grant allocation certificates providing for the importation of German **dyes** in amounts sufficient to supply the immediate requirements of individual consumers of the United States for a six months' period. (P. 1701)

The **chemical industry** of France continues to attract large amounts of capital and it is evident that it will become one of the leading industries of the country. The manufacture of synthetic camphor, sulfates of copper, and potash, and a trade-marked brand of butterine is receiving considerable attention from capitalists, as is also the distribution of petroleum, fuel, and lubricating oils. The soap and similar industries are expanding and many new companies are being formed. (P. 1720)

The **Norwegian** production in short tons of **copper ore** and **metal** from 1914 to 1917 was as follows:

	1914	1915	1916	1917
Copper pyrites	452,333	565,859	325,571	362,325
Nickel-copper ore	31,511	42,074	41,740	43,608
Other copper ore	63,880	61,836	31,603	43,318
Copper metal	3,152.2	3,116.2	1,279.6	1,995.2

(Pp. 1736–7)

The production of **minerals** in Algeria in 1919 shows a decline from the figures of 1918. (P. 1743)

It is reported that every essential for the successful development of the **tanning industry** in Venezuela is available and there are great opportunities open in this field which thus far has never really been exploited. (P. 1763)

The **sole leather** industry of France is reviewed, including statistics of imports and exports, characteristics of the French demand, domestic production of sole leather, methods of manufacture, principal producing centers, etc. (Pp. 1772–9)

By a decree of the Italian Ministry of Industry, Commerce, and Labor, maximum selling prices on different grades of **crude** and **refined Sicilian sulfur** are established, retroactively effective from May 1, 1920. (Pp. 1804–5)

Formal announcement has been made of a **merger** involving important **pulp** and **paper** properties in the Ottawa consular district, which affects 10,590 sq. m. of timber properties and limits in Ontario and Quebec, water powers aggregating 175,500 h. p., lumber mills with a present capacity of 125,000,000 ft board measure, and pulp and paper plants at present in operation with an annual capacity of 128,000 tons. (P. 1805)

SPECIAL SUPPLEMENTS ISSUED

FRANCE—7*a*
BRITISH INDIA—53*d*
JAPAN—58*a*
PERSIA—60*a*
SIAM—61*a*
NEW ZEALAND—64*a*
PORTUGUESE EAST AFRICA—75*a*

STATISTICS OF EXPORTS TO THE UNITED STATES

HANKOW—(P. 1579)
Antimony
Cottonseed oil
Wood oil
Sesame seed

HONGKONG—(P. 1252)
Peanut oil
Wood oil
Aniseed oil
Cassia oil (P. 1398–9)
Camphor
Peanut oil
Wood oil
Antimony
Chemicals
Aniseed oil
Cassia oil
Bismuth
Manganese
Wolfram
Paper
Tin

NANTES—(P. 1764)
Chemicals: crude glycerol
Fertilizers: animal carbon
Paints, pigments, etc.

ITALY—(P. 1382)
Olive oil
Citrus fruit essences
Citric acid
Tartaric acid
Citrate of lime
Crude tartar
Licorice root
Soap
Sumac
Colors
Raw and combined hemp
Artificial silk
Paper
Glue stock
Mercury
Crude and worked marble and alabaster
Pumice stone
Ordinary glasswares
Crude fiber and gutta percha

BAHIA—(P. 1495)
Chrome
Manganese
Rubber, india, crude
Wax, carnauba

LONDON—(P. 1709)
Drugs and chemicals
Gums
Tin
Leather
Aluminum
Linseed oil

JAPAN—(P. 1555)
Copra
Rubber (unmanufactured)
Oils:
  Coconut
  Peanut
  Rapeseed
  Soy bean

DUTCH EAST INDIES—(P. 1669)
Copra
Gum benzoin
Quinine
Quinine sulfate
Rubber
Tin
Wax, paraffin

BRAZIL AND PERU—(P. 1708)
Rubber

BOOK REVIEWS

Millions from Waste. By FREDERICK A. TALBOT. 308 pp. J. B. Lippincott Company, Philadelphia. F. Fisher Unwin, Ltd., London, 1920. Price, $5.00.

As the title of this work indicates, it treats of the value and possible financial returns to be derived from the proper utilization of waste of various descriptions and from various sources. The work is a most timely one and presents a subject of vital importance, especially in this reconstruction period. The subject, however, is treated entirely from the layman's standpoint and is largely devoted to the possibilities of the recovery of municipal, domestic, and household refuse, and only touches lightly upon the subject of the vast amount of waste occurring in industrial operations.

It is very unfortunate that the presentation of the subject matter of this work is so exceedingly verbose as to detract greatly from its value. After reading the book, one has the feeling of having struggled through a mass of high-sounding verbiage to get at the real facts which the author wishes to present. Some of the terminology has a purely local meaning and is not clearly understandable to the general reader. The author has treated the subject entirely from the British standpoint and its bearing upon conditions as they exist in England at the present time. One feature which might well be followed by other English writers, especially upon technical subjects, is the giving of monetary figures in both pounds sterling, and in dollars. There is another feature, however, which is open to severe criticism in work of this sort, and that is the repeated reference to a particular English firm's make of apparatus for dry solvent extraction and for multiple effect evaporation.

The work, however, shows evidence of much careful study of the subject, and effort on the part of the author in the accumulation of a great deal of interesting data upon the subject from a large number of sources. It contains much interesting information and some startling figures as to losses that are occurring every day in our domestic and municipal life through the neglect to utilize properly waste of various descriptions resulting therefrom. It would not seem that the chapter on the use of the electric lifting magnet, especially in its application to the handling of scrap metal, etc., is properly a part of a work of this sort, as the electric lifting magnet is merely a device for increasing the efficiency of operation in commercial plants.

A general brief discussion of the subject of waste occurring in every-day life is given; the author then passes to a discussion of what Germany and German interests have accomplished in the utilization of waste, even to the point of purchasing waste materials in other countries and shipping these waste material back to Germany, converting them into useful by-products, and in many instances selling these same by-products back to the country where the waste materials originated. It is clearly shown how Germany has developed the utilization of waste to a greater extent than any other country and how this worked out to her advantage during the war.

The author also takes up the measures that were adopted by the British Government to effect economies in the Commissary Department of the British Army and means that were employed to salvage all this from the army camps, and the results that were accomplished, especially in the production of fodder, fats, and glycerol.

There are then briefly described the developments that have taken place in the direction of new processes and apparatus for the proper carrying out of the conservation of waste materials, particularly as applied to organic refuse from which it is possible to extract fats and greases. It is surprising to learn how crude the methods are by which the efforts to utilize fish scrap in England have been carried out, in many cases the excess catches of fish not being rendered at all for the oil they contained but dumped directly on the land for fertilizing purposes. The author also shows how the slaughter-house and packing-house industries are lacking in their systems for recovery of their offal and how these industries in England particularly might be carried on along scientific lines, as is done in various foreign countries.

The great waste of paper is discussed particularly with its bearing upon the problem of the inadequate paper supply in England during the war, describing the measures that were adopted to help out in this emergency, and the various substitutes that were developed in the place of the large volumes of paper pulp which were normally imported.

The subject of domestic and municipal refuse is dealt with quite extensively and some very interesting figures are given as to the results which have been obtained in Liverpool, Bradford, and Oldham, England. It shows clearly the fallacy of the use of the destructor for the handling of municipal refuse, and the great values that are lost by such unscientific methods. The possibilities in the scientific handling of the various refuses and wastes occurring from the every-day life of the cities is set forth quite extensively.

The preparation of potatoes in a dried, powdered or flaked condition is urged as being one means of avoiding great losses in the food supply, and thereby effecting great economies for the ultimate consumer. The loss of fats and oils in soaps due to hard water is also set forth, and a full description given of a hard water soap made with a protein base, which prevents such loss.

The possibilities of the utilization of the various materials other than organic refuse, which are usually thrown into the dust can or garbage can, are also discussed. The author also advocates the distillation of all coal used for heating and steam-generating purposes, and shows what economies might be effected by such procedure. The gas and coke would be valuable for fuel purposes, and a very large gallonage of liquid fuel would be recovered as a substitute for the increasingly expensive gasoline for the motor fuel.

The various sources of fertilizer from waste materials is also indicated, such as from gas works, coke ovens, blast furnaces etc., as well as from some organic refuse such as banana stalks and wool-scouring liquors. The possibilities of recovery of sewage sludge are treated quite fully, and the results obtained in the cities of Bradford and Oldham, England, are described. Some interesting figures as to possible values are given; for instance, it is estimated that there might be recovered from the sewage sludge in England, annually, by-products of value to the amount of $175,000.00.

We in the United States, especially, have been a notoriously extravagant people in a large degree, consuming our natural raw materials with little regard for the conservation of our waste materials as a possible source of substitutes by the use of which to conserve our natural resources. This work is strongly recommended for reading by everyone interested in the slightest degree in bringing about a greater economy in our industrial and civic life. In spite of its verboseness, it would be a fund of information to those unfamiliar with this subject.

W. H. Dickerson

Military Pyrotechnics. 3 vols. By Henry B. Faber, Dean of the Pyrotechnic Schools, Ordnance Department, U. S. A. Illustrated. Government Printing Office, Washington, D. C.

Those who were in any way connected with the truly colossal pyrotechnic program inaugurated in the summer of 1918 by both the Army and Navy Departments in coöperation with the War Industries Board would have indeed welcomed at that time the three-volume treatise just issued by Dean Henry B. Faber of the Pyrotechnic Schools of the Ordnance Department. The unbelievably large item numbers connected with this program soon showed those working upon it that here was an industry which, at least at times, passed beyond the "Fourth of July" stage and assumed proportions of a first-class business. To produce the quantities of oxidizing agents, colorific salts and combustibles needed for these millions upon millions of signals which were to be called for, meant working many established industries to even more than full capacity and it also meant starting many new ones. Barium chlorate, arsenic sulfide, magnesium, phosphorus, tin salts, titanium compounds, dyes, etc., were called for in quantities hitherto undreamed of. The fabrication of these products into signals and screens meant revolutionary industrial changes in certain sections of the country. The Facilities Division of the War Industries Board was actively working on this problem at the time of the armistice.

It is to be hoped that no occasion for such enlarged production will ever again arise, but the fact that it might arise makes a study of the whole pyrotechnic field an essential part of preparedness for the future. This Dean Faber has done excellently well in these volumes. Here is considered the historical development of fire production and signal fires of all sorts and this is done so interestingly that even the layman would spend most entertaining hours reading those sections. Production of raw materials used in the industry is very thoroughly discussed in Volume III, although it is to be regretted in view of their importance in the war program that the production of magnesium and phosphorus was not taken up in detail. Perhaps the most useful of all is Volume II, in which is described the manufacture of the various types of military pyrotechnics, the material and machinery used and the latest methods of assembly.

Literature on all these phases of the industry was scattered and hard to locate, but the manufacturing methods were previously least well described and collected.

The vast amount of information included in the three volumes is all well arranged and available by good indexing. These books are a real contribution to the literature of applied chemistry and will be welcomed by all who work along these lines.

Herbert R. Moody

Food Inspection and Analysis. For the Use of Public Analysts, Health Officers, Sanitary Chemists and Food Economists. By Albert E. Leach, S.B., late Chief of the Denver Food and Drug Inspection Laboratory. Revised and Enlarged by Andrew L. Winton, Ph.D., formerly Chief of the Chicago Food and Drug Laboratory, Bureau of Chemistry, U. S. Department of Agriculture. 4th Edition. 1090 pp. 129 figures. 41 full page microphotographic plates. John Wiley & Sons, Inc., New York. Price, cloth, $8.50.

The appearance of a fourth edition of this standard work will be greatly welcomed. The first edition of Leach was published 15 years ago at the time of the establishment of the Food and Drugs Act, when the work of the food chemist was more largely applied to the detection of adulteration. During the last decade food analysis has tended, however, more from inspection to research, with the fortunate result that food chemists are becoming better scientists than detectives. Dr. Winton in the successive revisions of the work of his deceased friend and co-worker has very properly, therefore, laid increasing stress upon the applications of food analysis in other directions than mere inspection. Yet in so doing he has retained the same general method of presentation and the same sequence of chapters as in the earlier editions.

The revision has been performed by Dr. Winton in his customary conscientious and painstaking manner. Considerable new material has been added or substituted for that in previous editions, with the result that the present volume is brought thoroughly up-to-date, and contains 90 more pages than the previous printing. A special feature of the new edition is a timely chapter by Prof. G. L. Wendt on the determination of acidity by the hydrogen electrode, a method which is constantly finding new applications in food analysis. The greater attention given to footnote references in the present work will be of great assistance to those who desire to consult the original authorities.

The same excellent quality of typography and binding which characterized previous editions is maintained in the present work. The book for a volume of its size is exceptionally free from typographical errors. It is destined to retain for many years the important place which it has so worthily occupied.

C. A. Browne

Metallography. Part I, Principles of Metallography. By Samuel L. Hoyt, E.M., Ph.D., Metallurgical Engineer, National Lamp Works of General Electric Co.; formerly Associate Professor of Metallography, University of Minnesota. 1st Edition. x + 256 pp. McGraw-Hill Book Co., Inc., New York, 1920. Price, $3.00 net.

This book is the outgrowth of a course of lectures given at the University of Minnesota, and reflects not only the author's experience as a teacher but also his practical experience. This is the first of three volumes and is confined to principles only. The author discusses the constitution diagrams from the point of view of the phase rule and does it consistently throughout, not giving it mere mention to satisfy one's conscience, as is so frequently done. The whole book is treated in a thoroughly scientific manner, is concise and accurate. One could well wish that there might have been more detailed discussion in many places, but this the author will probably do in the forthcoming volumes on the Metals and Common Alloys, and Technical Practice.

The following chapter headings give an idea of the contents: I—Constitution Diagrams. II—The Preparation of Metallic Alloys. III—Metallic Microscopy. IV—The Microstructure of Metals and Alloys. V—Pyrometry and Thermal Analysis. VI—Physical Properties.

Under each chapter heading are discussed the subjects which have a bearing upon the more general title, the author always adhering to the principles involved, and presenting only those facts which have a bearing upon the scientific rather than the commercial side. The book could have been made more interesting by a change of sequence of the chapters and at the same time have maintained the continuity of the subject. The reviewer believes a more logical sequence of presentation would be to present the chapters in the following order: II, V, I, III, IV, and VI.

Henry Fay

Boiler Feed Water. A concise Handbook of Water for Boiler Feeding Purposes (Its Effects, Treatment, and Analysis). By Percy C. Jackson, F.I.C., formerly chemist to the National Boiler and General Insurance Company, Ltd. ix + 97 pp. Charles Griffin and Co., Ltd., London. J. B. Lippincott Co., Philadelphia, 1919. Price, $2.00.

The author states that this book is not intended to "explain theoretically why various constituents of feed water cause certain undesirable results, but only how experience has shown that these undesirable results may be eliminated, or at least mitigated."

Aside from an introductory chapter, this book has short chapters on the following topics: Mineral constituents; corrosion; softening; selection of softening plants; priming; scale, grease, and overheating; methods of analysis; analysis of scale; control tests for water softening; sampling; and solutions. It contains no illustrations or figures.

The book is short and concise, appears to be well written, and might prove to be very useful to some engineers and chemists who have to work on boiler feed water troubles. The average American industrial chemist or chemical engineer will find little that is new or novel to him, but as the material is collected in a small volume, the book may prove of value to those interested in its special province.

Francis J. Pond

Manual of Cyanidation. By E. M. Hamilton. 1st Edition. McGraw-Hill Book Co., Inc., New York, 1920. Price, $3.00 net.

This manual is everything that would be expected of it by those who know the author or who have had personal knowledge of the high standard of engineering work he has done and his broad knowledge of the subject. While it is necessarily to a large extent a compilation, it is illumined throughout by his wide experience and good judgment, and those portions detailing his own experience are not the least valuable.

The advantage of feeling no obligation to include the complete history of the art has meant the elimination of a mass of obsolete information; and considering the time required for the preparation of such a work, it is as up-to-the-minute as can well be. The index—covering 22 pages—places all the contents ready for immediate reference by student or operator, and will be greatly appreciated. The book will be regarded as a necessity by all connected with cyanidation—from manager to shiftman, and both the student and those engineers not directly connected with the industry, but who may occasionally be called on for information regarding it, can find no better source of information.

The notes on the chemistry of the process are compact yet comprehensive. The data on comparative results between so-called 98 per cent KCy and sodium cyanide are most interesting, and suggest either the effect of psychology on metallurgy or that the sodium cyanide originally marketed contained some compound that interfered with extraction or increased cyanide decomposition. I believe Mr. Allen Clark, consulting metallurgist for the Homestake Mining Co., tried sodium cyanide when it was first brought out, and abandoned it on account of lower extractions. A few years later, he tried it again and with no known change in conditions obtained the opposite result. This led to the opinion that a technical manager could profitably check over all his test work every few years, just as he should make every step in his flow sheet justify itself at intervals in the light of changed conditions. This is perhaps analogous to Bernard Shaw's idea, that a man should be obliged to justify his right to existence and his position every seven years, and not live on the past.

The chapter on "Testing and Analysis of Solutions" is complete. In giving four methods of solution assay without indicating his preference to stating which is most generally used, an easy opportunity to render the book more valuable was overlooked. My own recollection is that we passed through the first three methods and ended, as most operators have done, by using the fourth.

Sand Leaching and its adjunct, "Separation of Slime from the Sand," is not of great interest in North America, as I believe only two plants are using it. Although leaching has been practically abandoned here, it is still standard practice in South Africa—the largest gold producer of the world, which amply justifies the space iven. Production of a slime-free, leachable sand has always been the difficult problem. It is solved in South Africa by the Caldicott cone; at the Homestake by the Merrill cone system installed when the plants were built 15 years ago; and at the Golden Cycle by the Dorr bowl classifier which has within the last few years replaced the Dorr classifiers formerly used. This machine has increased the leaching rates to 9.5 in. per hour, or three times the rate Mr. Hamilton gives as satisfactory. The writer hesitates in speaking of apparatus in which he is commercially interested, but personality is unimportant. It is evident Mr. Hamilton was unfamiliar with this apparatus and its work, as he has suggested a Dorr washing classifier for the same purpose.

Slime treatment has always been of the greatest importance—originally because it presented the greatest obstacles to success and was the cause of large losses, and now because, except in South Africa, all-sliming is the customary treatment. Mr. Hamilton has devoted much space to it and gives excellent theoretical and practical information covering slime settlement, dissolution of metals, and their separation by continuous counter-current decantation or filtration. While generalizing very ably, he has not attempted to approach the difficult question of losses of dissolved value to the tailings.

The chapter on the discrepancies between actual recovery and theoretical extraction will prove of the greatest help to operators who have to meet that situation and to the student as well.

Precipitation has been covered very completely with ample data regarding the use of zinc shavings, zinc dust, and electrolytic work. Full details are given on aluminum precipitation and the use of sodium sulfide, rendered necessary by the war-time shortage and high cost of aluminum, is covered. It is interesting to note that charcoal used as a precipitant in the early days of cyaniding has been tried again in Australia. The advances in chemical knowledge due to study necessitated by gas warfare may open great possibilities in this line, although zinc dust precipitation with the Crowe vacuum process sets a high mark in convenience and low operating costs at normal zinc prices.

J. V. N. Dorr

NEW PUBLICATIONS

Chemistry: Laboratory Outline of General Chemistry. H N. McCoy and E. M. Terry. 154 pp. 20 illustrations. Price, $1.25. McGraw-Hill Book Co., Inc., New York.

Colloids: Grundriss d. Kolloidchemie. Wo. Ostwald. 5th Ed. Part 1. Price, 18 mk. Dunod, Paris.

Combustion: Méthodes Economiques de Combustion dans les Chaudières à Vapeur. J. Izart. 4th Ed., revised. 383 pp. Price, 25 Fr.50. Dunod, Paris.

Dyes: Natural Organic Colouring Matters. Arthur G. Perkin. 656 pp. Price, $9.50. Longmans, Green & Co., New York.

Electrochemistry: The Principles of Applied Electrochemistry. A. J. Allmand. 2d Impression. 547 pp. Price, $8.00. Longmans, Green & Co., New York.

Enzymes: Biochemical Catalysts in Life and Industry: Proteolytic Enzymes. Jean Effront. Translated by Samuel C. Prescott. 752 pp. Price, $5.00. John Wiley & Sons, Inc., New York.

Handbook: Recipes, Formulas, and Processes. G. D. Hiscox, Editor. 800 pp. Price, $4.00. The N. W. Henley Pub. Co , New York.

Handbook: The Chemists' Year Book. Edited by F. W. Atack, assisted by L. Whinyates. Vols. I and II. 1136 pp. Price, $7.50. Sherratt & Hughes, Manchester, Eng.; Longmans, Green & Co., New York.

History: A History of Chemistry. J. Campbell Brown. 2d Ed. 544 pp. Price, $6.00. P. Blakiston's Son & Co., Philadelphia, Pa.

Hydrogen Ions: Determination of Hydrogen Ions. W. Mansfield Clark. 325 pp. Price, $5.00. Williams & Wilkins Co., Baltimore.

Metallography of Steel and Cast Iron. Henry M. Howe. 641 pp. Price, $10.00. McGraw-Hill Book Co., Inc., New York.

Peat: Peat Industry Reference Book. Frederick T. Gissing. 292 pp Price, $3 00. Charles Griffin & Co., Ltd., London.

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By-Product Coke: Recent By-Product Coke Oven Developments. J. Becker and F. W. Sperr, Jr. *Blast Furnace and Steel Plant*, Vol. 8 (1920), No. 6, pp. 330–337.

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Coal: Powdered Coal Efficiencies. H. D. Savage. *The Gas Age*, Vol. 45, (1920), No. 12, pp. 541–543.

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MARKET REPORT—JULY, 1920

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

		July 1	July 15
Acid, Boric, cryst., bbls.	lb.	.18	.18
Hydrochloric, com'l, 22°	lb.	.03½	.03½
Hydriodic	oz.	.19	.19
Nitric, 42°	lb.	.08½	.08½
Phosphoric, 50% tech	lb.	.25	.25
Sulfuric, C. P.	lb.	.07	.07
Chamber, 66°	ton	22.00	22.00
Oleum	ton	28.00	28.00
Alum, ammonia, lump	lb.	.04	.04
Aluminum Sulfate (iron-free)	lb.	.04¼	.05
Ammonium Carbonate, pwd	lb.	.16	.16
Ammonium Chloride, gran	lb.	.15	.15
Ammonia Water, carboys, 26°	lb.	.12	.10
Arsenic, white	lb.	.15	.16
Barium Chloride	ton	170.00	170.00
Nitrate	lb.	.11	.11
Barytes, white	ton	30.00	30.00
Bleaching Powd., 35%, Works,	100 lbs.	6.00	6.00
Borax, cryst., bbls	lb.	.10	.10
Bromine, tech., bulk	lb.	.85	.85
Calcium Chloride, fused	ton	27.50	27.50
Chalk, precipitated, light	lb.	.05	.05
China Clay, imported	ton	18.00	18.00
Copper Sulfate	100 lbs.	8.25	8.25
Feldspar	ton	8.00	8.00
Fuller's Earth	100 lbs.	1.25	1.25
Iodine, resublimed	lb.	4.35	4.35
Lead Acetate, white crystals	lb.	.15	.15
Nitrate	lb.	.15	.15
Red American	100 lbs.	.10½	.10½
White American	100 lbs.	.09½	.09½
Lime Acetate	100 lbs.	3.50	3.50
Lithium Carbonate	lb.	1.50	1.50
Magnesium Carbonate, Tech	lb.	.12	.12
Magnesite	ton	65.00	65.00
Mercury flask	75 lbs.	90.00	90.00
Phosphorus, yellow	lb.	.35	.35
Plaster of Paris	100 lbs.	1.50	1.50
Potassium Bichromate	lb.	.44	.44
Bromide, Cryst	lb.	.95	.95
Carbonate, calc., 80–85%	lb.	.18	.18
Chlorate, cryst	lb.	.16	.16
Cyanide, bulk, 98–99%	lb.	.30	.30
Hydroxide, 88–92%	lb.	.32	.30
Iodide, bulk	lb.	3.35	3.35
Nitrate	lb.	.14	.15
Permanganate, U. S. P.	lb.	.85	.80
Salt Cake	ton	40.00	40.00
Silver Nitrate	oz.	.58	.60
Soapstone, in bags	ton	12.00	12.00
Soda Ash, 58%, bags	100 lbs.	3.65	3.25
Caustic, 76%	100 lbs.	6.25	6.00
Sodium Acetate	lb.	.12	.12
Bicarbonate	100 lbs.	3.00	3.00
Bichromate	lb.	.27	.24
Chlorate	lb.	.12	.12
Cyanide	lb.	.27	.27
Fluoride, technical	lb.	.18	.18
Hyposulfite, bbls	100 lbs.	3.60	3.70
Nitrate, 95%	100 lbs.	3.85	3.90
Silicate, 40°	lb.	.02	.02
Sulfide	lb.	.10¼	.10¼
Bisulfite, powdered	lb.	.06½	.06½
Strontium Nitrate	lb.	.17½	.15
Sulfur, flowers	100 lbs.	3.75	4.00
Crude	long ton	25.00	25.00
Talc, American, white	ton	20.00	20.00
Tin Bichloride	lb.	.21½	.21½
Oxide	lb.	.60	.60
Zinc Chloride, U. S. P.	lb.	.50	.50
Oxide, bbls	lb.	.12	.12

ORGANIC CHEMICALS

		July 1	July 15
Acetanilid	lb.	.75	.70
Acid, Acetic, 28 p. c.	100 lbs.	4.00	4.00
Glacial	lb.	.15½	.14
Acetylsalicylic	lb.	.95	.92
Benzoic, U. S. P., ex-toluol	lb.	.85	.85
Carbolic, cryst., U. S. P., drs.	lb.	.15	.15
50- to 110-lb. tins	lb.	.23	.24
Acid (*Concluded*)			
Citric, crystals, bbls	lb.	.85	.80
Oxalic, cryst., bbls	lb.	.60	.60
Pyrogallic, resublimed	lb.	2.50	2.50
Salicylic, bulk, U. S. P.	lb.	.55	.55
Tartaric, crystals, U. S. P.	lb.	.78	.76
Trichloracetic, U. S. P.	lb.	4.40	4.40
Acetone, drums	lb.	.22	.22
Alcohol, denatured, 190 proof	gal.	1.13	1.13
Ethyl, 190 proof	gal.	7.00	7.00
Wood, Pure	gal.	4.40	4.40
Amyl Acetate	gal.	4.00	4.00
Camphor, Jap. refined	lb.	1.40	1.25
Carbon Bisulfide	lb.	.08	.08
Tetrachloride	lb.	.14½	.14½
Chloroform, U. S. P.	lb.	.40	.40
Creosote, U. S. P.	lb.	.75	.75
Cresol, U. S. P.	lb.	.18	.18
Dextrine, corn	lb.	.07½	.07½
Imported Potato	lb.	.11	.12
Ether, U. S. P., conc., 100 lbs	lb.	.24	.24
Formaldehyde	lb.	.51	.51
Glycerol, dynamite, drums	lb.	.27	.27
Pyridine	gal	2.75	2.75
Starch, corn	100 lbs.	5.75	5.75
Potato, Jap.	lb.	.06½	.06½
Rice	lb.	.25	.25
Sago	lb.	.05	.05

OILS, WAXES, ETC.

		July 1	July 15
Beeswax, pure, white	lb.	.60	.60
Black Mineral Oil, 29 gravity	gal.	.22	.22
Castor Oil, No. 3	lb.	.18	.18
Ceresin, yellow	lb.	.16	.16
Corn Oil, crude	lb.	.16	.16
Cottonseed Oil, crude, f. o. b. mill	lb.	.16	.16
Menhaden Oil, crude (southern)	gal.	.70	.70
Neat's-foot Oil, 20°	gal.	2.00	2.00
Paraffin, 128–130 m. p., ref	lb.	.11½	.11½
Paraffin Oil, high viscosity	gal.	.45	.45
Rosin, "F" Grade, 280 lbs	bbl.	16.25	15.95
Rosin Oil, first run	gal.	.70	.67
Shellac, T. N.	lb.	1.15	1.20
Spermaceti, cake	lb.	.30	.30
Sperm Oil, bleached winter, 38°	gal.	1.95	1.95
Stearic Acid, double-pressed	lb.	.27½	.25½
Tallow Oil, acidless	gal.	1.60	1.60
Tar Oil, distilled	gal.	.60	.60
Turpentine, spirits of	gal.	1.52½	1.57½

METALS

		July 1	July 15
Aluminum, No. 1, ingots	lb.	.32	.32
Antimony, ordinary	100 lbs.	8.00	7.75
Bismuth	lb.	2.72	2.72
Copper, electrolytic	lb.	.18½	.18
Lake	lb.	.18½	.18½
Lead, N. Y.	lb.	.08½	.08½
Nickel, electrolytic	lb.	.45	.45
Platinum, refined, soft	oz.	80.00	80.00
Quicksilver, flask	75 lbs ea.	90.00	90.00
Silver	oz.	1.00	1.00
Tin	lb.	.50	.50½
Tungsten Wolframite	per unit	6.50	6.50
Zinc, N. Y.	100 lbs.	8.00	7.75

FERTILIZER MATERIALS

		July 1	July 15
Ammonium Sulfate	100 lbs.	6.50	6.05
Blood, dried, f. o. b. N. Y.	unit	8.00	8.00
Bone, 3 and 50, ground, raw	ton	48.00	48.00
Calcium Cyanamide, unit of Ammonia		4.00	4.00
Fish Scrap, domestic, dried, f. o. b. works	unit	7.25	7.25
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%	ton	6.85	6.85
Tennessee, 78–80%	ton	11.00	11.00
Potassium Muriate, 80%	unit	2.50	2.40
Pyrites, furnace size, imported	unit	.18	.18
Tankage, high-grade, f. o. b. Chicago	unit	7.75	7.75

COAL-TAR CHEMICALS

		July 1	July 15
Crudes			
Benzol, C. P.	gal.	.35	.35
Cresol, U. S. P.	lb.	.18	.18
Naphthalene, flake	lb.	.18	.18
Phenol, drums	lb.	.15	.15
Toluol, 90%	gal.	.35	.35
Xylol, water white	gal.	.40	.40
Intermediates			
Acids:			
Anthranilic	lb.	2.05	2.05
B	lb.	2.25	2.25
Benzoic	lb.	.85	.85
Broenner's	lb.	1.75	1.75
Cleves	lb.	2.00	2.00
Cresylic, 97–99%	gal.	1.20	1.20
F.	lb.	3.50	3.50
Gamma	lb.	2.50	2.50
H	lb.	2.25	2.25
Metanilic	lb.	1.70	1.70
Monosulfonic F	lb.	3.50	3.50
Napthionic, crude	lb.	.85	.85
Nevile & Winther's	lb.	1.90	2.00
Phthalic	lb.	.60	.60
Picric	lb.	.25	.25
Sulfanilic	lb.	.35	.37
Tobias	lb.	2.25	2.25
Amido Azo Benzol	lb.	1.15	1.15
Aniline Oil	lb.	.33	.33
For Red	lb.	.65	.65
Aniline Salt	lb.	.38	.40
Anthracene, 80–85%	lb.	.75	.75
Anthraquinone	lb.	4.50	4.50
Benzaldehyde, tech.	lb.	.65	.65
U. S. P.	lb.	1.00	1.00
Benzidine Base	lb.	1.40	1.40
Benzidine Sulfate	lb.	1.15	1.15
Diamidophenol	lb.	6.00	6.00
Dianisidine	lb.	9.00	9.00
p-Dichlorbenzol	lb.	.10	.10
Diethylaniline	lb.	1.75	1.75
Dimethylaniline	lb.	1.25	1.30
Dinitrobenzol	lb.	.36	.36
Dinitrotoluol	lb.	.43	.43
Diphenylamine	lb.	.80	.80
G Salt	lb.	.90	.90
Hydroquinone	lb.	2.10	2.25
Metol (Rhodol)	lb.	6.75	6.75
Monochlorbenzol	lb.	.18	.18
Monoethylaniline	lb.	2.15	2.15
a-Naphthylamine	lb.	.55	.55
b-Naphthylamine (Sublimed)	lb.	2.25	2.25
b-Naphthol, crude	lb.	.86	.88
m-Nitraniline	lb.	1.05	1.05
p-Nitraniline	lb.	1.50	1.40
Nitrobenzol, crude	lb.	.14	.14
Rectified (Oil Myrbane)	lb.	.18	.18
p-Nitrophenol	lb.	.80	.80
p-Nitrosodimethylaniline	lb.	2.90	2.90
o-Nitrotoluol	lb.	.25	.25
p-Nitrotoluol	lb.	1.50	1.50
m-Phenylenediamine	lb.	1.15	1.15
p-Phenylenediamine	lb.	2.60	2.55
Phthalic Anhydride	lb.	.45	.50
Primuline Base	lb.	3.00	3.00
R Salt	lb.	.90	.90
Resorcin, tech.	lb.	3.50	3.50
U. S. P.	lb.	5.50	5.25
Schaeffer Salt	lb.	.75	.75
Sodium Naphthionate	lb.	1.10	1.10
Thiocarbanilid	lb.	.60	.60
Tolidine, Base	lb.	1.75	1.75
Toluidine, mixed	lb.	.44	.44
o-Toluidine	lb.	.35	.35
m-Toluylenediamine	lb.	1.40	1.40
p-Toluidine	lb.	2.00	2.00
Xylidene, crude	lb.	.45	.45

COAL-TAR COLORS

		July 1	July 15
Acid Colors			
Black	lb.	1.15	1.15
Blue	lb.	3.00	3.00
Acid Colors (*Concluded*)			
Fuchsin	lb.	2.50	3.00
Orange III	lb.	1.00	1.00
Red	lb.	1.10	1.30
Violet 10B	lb.	6.50	6.50
Alkali Blue, domestic	lb.	4.75	5.50
Imported	lb.	8.00	8.00
Azo Carmine	lb.	4.00	4.00
Azo Yellow	lb.	2.00	2.00
Erythrosine	lb.	12.00	12.00
Indigotine, conc.	lb.	3.00	3.00
Paste	lb.	1.50	1.50
Naphthol Green	lb.	1.50	1.50
Ponceau	lb.	1.25	1.35
Scarlet 2R	lb.	1.00	1.00
Direct Colors			
Black	lb.	1.00	1.00
Blue 2B	lb.	.70	.70
Brown R	lb.	1.80	1.80
Fast Red	lb.	3.50	3.50
Yellow	lb.	2.00	2.00
Violet, con't	lb.	2.20	2.20
Chrysophenine, domestic	lb.	2.25	2.25
Imported	lb.	3.80	3.80
Congo Red, 4B Type	lb.	.90	.90
Primuline, domestic	lb.	3.00	3.00
Oil Colors			
Black	lb.	.70	.70
Blue	lb.	1.65	1.65
Orange	lb.	1.40	1.40
Red III	lb.	1.65	1.65
Scarlet	lb.	1.75	1.75
Yellow	lb.	1.70	1.70
Nigrosine Oil, soluble	lb.	.90	.90
Sulfur Colors			
Black	lb.	.20	.20
Blue, domestic	lb.	.70	.70
Brown	lb.	.35	.35
Green	lb.	1.00	1.00
Yellow	lb.	.90	.90
Chrome Colors			
Alizarin Blue, bright	lb.	7.75	7.75
Alizarin Red, 20% Paste	lb.	1.10	1.10
Alizarin Yellow G	lb.	1.00	1.00
Chrome Black, domestic	lb.	1.25	1.25
Imported	lb.	2.20	2.20
Chrome Blue	lb.	2.50	2.50
Chrome Green, domestic	lb.	1.50	1.50
Chrome Red	lb.	2.00	2.00
Gallocyanine	lb.	3.25	3.25
Basic Colors			
Auramine, O, domestic	lb.	2.50	2.50
Auramine, OO,	lb.	4.15	4.15
Bismarck Brown Y	lb.	.90	.90
Bismarck Brown R	lb.	1.20	1.20
Chrysoidine R	lb.	.75	.75
Chrysoidine Y	lb.	.75	.75
Green Crystals, Brilliant	lb.	6.00	6.00
Indigo, 20 p. c. paste	lb.	.85	.85
Fuchsine Crystals, domestic	lb.	5.00	5.50
Imported	lb.	12.00	12.00
Magenta Acid, domestic	lb.	4.25	4.25
Malachite Green, crystals	lb.	4.50	4.50
Methylene Blue, tech.	lb	2.50	2.75
Methyl Violet 3 B	lb	3.00	3.50
Nigrosine, spts. sol.	lb.	.85	.85
Water sol., blue	lb.	.65	.65
Jet	lb	.90	.90
Phosphine G., domestic	lb.	7.00	7.00
Rhodamine B. extra conc'd	lb.	35.00	40.00
Victoria Blue, base, domestic	lb	6.00	6.00
Victoria Green	lb	6.00	6.00
Victoria Red	lb.	7.00	7.00
Victoria Yellow	lb	7.00	7.00

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CONTENTS

EDITORIALS:

Increase the Dues 834
Potash from a New Angle 834
Chairman Bancroft's Report 835
Crippling a Great Work 835
Mutual Obligations 836
THE UNITED STATES' SEARCH FOR NATURAL DEPOSITS OF SOLUBLE POTASH. H. D. Ruhm 837
OUR FOREIGN TRADE IN CHEMICALS. O. P. Hopkins 840

ORIGINAL PAPERS:

The Direct Synthetic Ammonia Process. R. S. Tour 844
Gasoline from Natural Gas. III—Heating Value, Specific Gravity, and Specific Heat. R. P. Anderson 852
Alkali Fusions. II—The Fusion of Sodium Benzene *m*-Disulfonate with Sodium Hydroxide for the Production of Resorcinol. Max Phillips and H. D. Gibbs 857
The Prevention of Sugar Deterioration by the Use of Superheated Steam in Centrifugals. Nicholas Kopeloff 860
The Cause and Prevention of After-Corrosion on the Bores of Firearms. Wilbert J. Huff 862
Strength and Velocity of Detonation of Various Military Explosives. W. C. Cope 870
Some Observations on the Determination of Cellulose in Woods. S. A. Mahood 873
The Determination of True Free Sulfur and the True Coefficient of Vulcanization in Vulcanized Rubber. W. J. Kelly 875
Determination of the Jellying Power of Gelatins and Glues by the Polariscope. C. R. Smith 878
Some Physical Constants of Pure Aniline. C. L. Knowles 881
The Detection and Estimation of Yellow AB and Yellow OB in Mixtures. Walter E. Mathewson 883
Determination of Sulfur Forms in Coal. Alfred R. Powell 887
The Diffusing Power of Pigments. W. K. Lewis and F. P. Baker 890

LABORATORY AND PLANT:

The Determination of the Specific Heat of Heavy Mineral Oils. Herbert S. Bailey and Carlton B. Edwards 891
The Application of the Thermal Conductivity Method to the Automatic Analysis of Complex Mixtures of Gases. E. R. Weaver and P. E. Palmer 894
Laboratory Control of Wheat Flour Milling. Benjamin R. Jacobs and Olaf S. Rask 899
Welding Thermocouples in the Electric Arc. James C. McCullough 903
THE WATER SUPPLY OF THE AMERICAN EXPEDITIONARY FORCES. Edward Bartow 903
IMPRESSIONS OF THE ITALIAN CHEMICAL INDUSTRY 907

ADDRESSES AND CONTRIBUTED ARTICLES:

Indexing References. Alfred Tingle 909
Wood Alcohol No Longer: Hereafter Methanol. Charles Baskerville 910

SCIENTIFIC SOCIETIES:

National Research Council—Report of the Chairman at the Annual Meeting of the Division of Chemistry and Chemical Technology; Setting the Scenes for the Chicago Meeting; Sixth National Exposition of Chemical Industries, Grand Central Palace, New York, September 20 to 25, 1920; Report of the Committee on Legislation of the American Dyes Institute; American Ceramic Society and British Society of Glass Technologists; Chemical Warfare Post of the American Legion; Calendar of Meetings 911
THE INTERNATIONAL CHEMICAL CONFERENCE 925
WASHINGTON LETTER 926
LONDON LETTER 928
INDUSTRIAL NOTES 929
PERSONAL NOTES 930
GOVERNMENT PUBLICATIONS 930
NEW PUBLICATIONS 934
MARKET REPORT 935

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EDITORIALS

INCREASE THE DUES

A paragraph in the preliminary program of the Chicago meeting calls attention to an important matter which concerns directly every member of the American Chemical Society, namely, the possibility that the steadily mounting cost of conducting the Society's business will necessitate an increase in membership dues. To this subject the Council will give earnest consideration at its meeting on September sixth.

To each member who has paid $10.00 for the year 1920 the Society will have furnished publications costing at least $12.24 per member, exclusive of the cost of printing the advertising sections, according to the appropriations already made by the Directors and the latest available membership figure. We know from our own increase in the cost of printing since our budget estimate was made that at least 30 cents per member will have to be added to cover that item alone. It is safe to say that the printing costs of This Journal alone for the year 1921 will be not less than 40 cents per member above the figure estimated for 1920.

Other activities of the Society have brought the total cost per member, based upon figures in the minutes of the meetings of the Directors, to $15.60, exclusive of the expenses in connection with the Society's advertising business, the net income from which must be relied upon largely to meet the excess of expenditures. But a continuation of this policy would mean plunging into a sea of reckless financing.

There is but one alternative to an immediate increase in dues, namely, the adoption of a policy of stringent curtailment of activity, both in the publication field and in the Society's various other lines of usefulness. The policy of expansion of This Journal unanimously adopted in 1916 might be revoked; the A. C. S. News Service might be abolished, just at the moment when it is proving beyond the shadow of a doubt that it is performing an essential function in the life of the Society and of the nation; the scope of *Chemical Abstracts* might be narrowed; indeed, each item of the annual budget, always conservatively defined by the Directors, might be contracted. But this is no time for retrenchment. The country is awakening as never before to the meaning of chemistry in everyday life; the capital invested in the chemical industries is far greater than at any period in our history; legislation, enacted and in the making, recognizes the importance of chemistry as a national asset. Shall it be said that at this constructive period in the development of American chemistry the American Chemical Society has had to restrict its activities because of lack of funds?

From the point of view of the individual members, on the other hand, the proposed increase to $15.00 should not exclude the younger chemists, on whom it has been argued that an additional assessment would be a burden. These young men are to-day receiving practically double what the man with the same training and attainments received a few years ago. The increased rate, therefore, would mean a smaller percentage expenditure of income than was the ten-dollar figure before the war. While the higher salaried man may not have received a proportionate increase in salary, the question of one five-spot more or less, annually, is not a serious matter to him.

To curtail activity is false policy; to gamble on hoped-for income is poor finance. To insure to the Society a future of still greater service, an increase of dues is absolutely necessary.

POTASH FROM A NEW ANGLE

An entirely new phase of the potash question is discussed in the interesting article by Mr. H. D. Ruhm on pages 837–840 of this issue. In connection with the possibilities of discovering in this country natural deposits corresponding to those in Germany and in Alsace, he points out clearly the all too limited extent of our past explorations by borings, our faulty methods of taking out cores, and the unsound economics in confining the search largely to western areas far removed from the centers of fertilizer consumption, while the great salt deposits of New York, Ohio, and Michigan (and, we would like to add, southwest Virginia and Louisiana) remain unexplored. We hope Mr. Ruhm's article will receive earnest consideration. It is not difficult to read between the lines the inference that America's complacent inactivity may have been fostered by German propaganda.

When we think of the prevailing conviction that no potash deposits like those of Germany exist in this country, we cannot but remember that when legislation was first proposed to develop an American dye industry a hue and cry was immediately raised that American coal was not suited to dye manufacture. It sounds funny now, but the thought gained such hold that it required several really serious statements to clear up the point before Congressional committees.

We may not be strong on geology, but we hold three convictions very strongly:

First—Potash was leached out of our original rocks when the great clay beds of America were formed, just as it is being leached out to-day.

Second—We believe that diffusion of salts in aqueous solution is alike the world over and showed no tendency to pile up potash in the neighborhood of what was destined to be Stassfurt and adjacent cities.

Third—The laws of deposition from saturated solutions need no guarantee of territorial integrity; they are world-wide in their application.

With these elementary thoughts in mind we go the full length with Mr. Ruhm in urging that more extensive, more intelligent, and better located efforts be made to determine by fact, rather than by suggested negation, whether or not there are rich stores of potash in the vicinity of our great salt deposits.

What a pitiful story is this whole American potash question! The statistics of production, as given by the U. S. Geological Survey, are as follows:

YEAR	FIRMS	TONS OF K_2O	VALUE
1915	5	1,090	$ 342,000
1916	70	9,720	4,242,730
1917	95	32,573	13,980,577
1918	128	54,803	15,839,618
1919	73	30,899	7,889.440
1920 (3 mo.)	43	11,969	2,738,195

A rapid increase in output took place from 1916 to the end of 1918, with all indications of further increase in 1919. Fearing German importations, the potash producers asked protection of Congress. Mr. Fordney, chairman of the Ways and Means Committee, introduced a bill, embodying a form of restricted license, but the objurgations of his fellow Republicans and the gibes of his Democratic colleagues forced his return to the accustomed waters of protection-through-tariff-alone.

Farmers fought the bill because they didn't want any kind of protection for the American potash industry, they wanted the "good old cheap German potash" again. They haven't got it yet by a long sight and will not for many, many years, unless a strong American industry can force the price down. The American Commissioner in Berlin has cabled that the Germans are selling potash to America at prices varying from $108 to $122, according to time of delivery, while they charge Holland only $50. The German will get all the money out of America he possibly can for his potash, and so will the Frenchman.

The fertilizer manufacturers did not support the bill. They were interested in German mines. On June 9, 1920, the *New York Times* published the following:

> Corporation Councilor Maximilian Kemptner, who is probably the greatest expert on the potash industry, informed the *Times* correspondent about American investments in that industry in Germany, chief among them being by the Virginia-Carolina Chemical Company, and the International Agricultural Chemical Company, which were interested respectively in the Einickeit and the Sollstedt potash works. Altogether the potash works in Germany have sold to America this year 250,000 tons of potash, which he hopes will be increased to 500,000 in the next eighteen months.

No indignant denials of this definite statement have come to our notice. Those 250,000 tons have not yet been delivered. Are they purposely to constitute a continuing threat against favorable legislation?

Meanwhile the American industry is convalescing. It was crippled last year by the unsympathetic attitude of a Congress dominated in both branches by the party which boasts of its policy of protection for American industries, and by the sly propaganda of expected large imports of German potash. But methods and product have been improved, and fear of cheap German potash has been dispelled.

What are we doing in a governmental way to aid this industry? Nothing! An appropriation to the Department of Agriculture amounting to $67,400 was voted by the last Congress to complete the kelp investigation at the experimental plant at Summerland, California—why? Because it was shown that the sale of the products made at the plant in 1920 would bring $101,000, while the estimated receipts in 1921 are expected to reach $223,000.

On the other hand, the country has been paying millions and millions of dollars of tribute for years for foreign potash, buying much more potash than was needed for certain soils, because of clever propaganda, protesting against, but ultimately acquiescing in, a German export tax which in one year's chunk mulcted this country of $15,000,000, and now buying again at figures which would have staggered the farmers five years ago. A small part of the millions of profits, which have been going and may continue to go to Germany, would enable a real exploration for potash in our great salt beds; legislation which practically fixed a price of not more than $2.50 a unit (the price now being paid) would encourage capital and enterprise in the industry.

We hark back to the words of Ambassador Pinckney, in 1796, "Millions for defense but not one cent for tribute."

CHAIRMAN BANCROFT'S REPORT

We are fortunate in securing for publication in this issue, pages 911–918, the report of Professor W. D. Bancroft, the retiring chairman of the Division of Chemistry and Chemical Technology of the National Research Council. The report is stimulating and inspiring in every feature. To the man beset with the humdrum of everyday routine, its reading will be like a breath of fresh air during a sultry day; for the man who thinks ahead, there will be found here a wealth of new material which should aid greatly in blazing the way for research.

The report in itself is a surety of the value of the National Research Council to the research activities of the nation. · One need not look below the surface to understand the fine results obtained from the chairman's contact with men in the allied sciences, and from the opportunity afforded by the character of the office to devote thought and energy exclusively to the problems of research. In this evident inauguration of real coördination and guidance of research along important lines there will no doubt be discovered the answer to some of the criticism which has been directed against university research.

The tenure of office of each chairman is limited to one year because it is desired to focus different types of mind upon the general question of research problems in chemistry. As these reports with their many-sided viewpoints accumulate, there should be cleared a pathway straight to the goal of truth, along which can march a host of workers. Professor Bancroft has proved himself a pioneer of sturdy type.

CRIPPLING A GREAT WORK

In a notable address in Baltimore, on September 30, 1918, Hon A. Mitchell Palmer, the then Alien Property Custodian, took the country into his confidence as to the threat against our public welfare which lay within the great industrial machine which Germany had quietly but with characteristic thoroughness coiled like a great viper about the vitals of this nation, and promised to rid America of the menace. The exposition of the danger and his determination to remove it rallied to his aid the services of the ablest lawyers and financiers in the land. And Judge Palmer made good his promises. Gradually the coils were unwound, through the seizure of the enemy-owned properties and their sale to American citizens. This great work was carried out in a manner which has successfully defied criticism either of a political or of a financial character. That was all the Alien Property Custodian could do.

The concomitant thought in this great piece of war work was that America should become economically independent of Germany as a source of certain essential supplies. In the great majority of cases the results have been admirable. American control, where once was German, is being exercised for America's good. Formerly not only were profits made for Germans, but frequently those very profits were turned to corruption in the practice of bribery and in the support of a complex system of espionage.

But there are indications that the fine work of Judge Palmer and his successor, Mr. Garvan, is being crippled by the action of American stockholders to whom some of these properties were sold under authorization of Congress. For example, the enemy-owned stock of the Kny-Scheerer Corporation (surgical instruments) was seized by the Alien Property Custodian, and on April 24, 1919, was sold to American citizens. The Alien Property Custodian's report to Congress, pages 120–121, stated:

> The president of the company is Richard Kny, whose activities I have had occasion to investigate in connection with the Chemical Exchange in the Heyden Chemical Co., the Eisemann Magneto Co., and the New York Patents Exploitation Corporation.
>
> * * * *
>
> Through the Bureau of Investigation in my office, a lengthy and careful examination [of the Kny-Scheerer Corporation] was had covering a period of months. It was discovered that information submitted for my inspection had been falsified, and that important instruments had been suppressed. Finally, the proof established by my bureau reached such proportions that Kny withdrew his claims of ownership and reported that the property was owned by Aktien Gesellschaft fur Fein Mechanik (commonly called A. G. F. M.).
>
> The investigation disclosed that A. G. F. M. had purchased the business from Kny in 1896, and that from that time Kny had simply been an employee of the German company. During an investigation conducted by the customs authorities into alleged undervaluations, and later in an attempt to evade the British blockade, the books and records of the Kny-Scheerer Corporation had been prepared so as to give it an appearance of an independent American company entirely free of foreign or German connections. When the trading-with-the-enemy act was passed, advantage was taken of this condition by Kny to make a bold and unscrupulous claim to the property, which finally was broken down by my office.

Nevertheless, Mr. Kny was retained as president for at least a year by the new American owners. Mr. E. S. Beck was likewise retained as secretary, and during that period we have been told that the manufacturing plant in Brooklyn was closed, while surgical instruments were again imported from Germany and offered to the trade in America at prices guaranteed to be 20 per cent below the prices of American goods. Mr. Kny has resigned the presidency, but we have not heard of any manufacturing operations in this country by that firm.

$3,000,000 of the preferred stock of the Susquehanna Silk Mills was owned by Germans and is now the property of the Alien Property Custodian, but as this stock has no voting power he found himself powerless to prevent the representative of this company from being extremely active in Washington opposing legislation whose sole purpose is the development of an American industry, necessarily to the injury of the German.

These are indications of failure of the ultimate purpose of the Custodian's work. Plainly, the remedy is effective protective legislation by Congress for bona fide American manufacturers whose products are faced with actual or at least potential destructive competition.

It is a strange commentary upon political affairs that the only instance of the passage by both House and Senate of protective legislation for an American industry from the beginning of the war to the present moment took place when both bodies were controlled by the Democrats. Since the Republicans gained control, none of the many bills introduced for this purpose have secured a favorable vote in the Senate. Senator Penrose dubs these bills "pop-gun legislation" and decrees that they must wait until a general revision of the tariff can be undertaken. Meanwhile, impending disaster waits at the door. The responsibility for its removal lies with the present Congress.

MUTUAL OBLIGATIONS

The organization of the General Meetings of the American Chemical Society offers unusual opportunity for the oral presentation of the results of research. The Society includes upon its program the name of the author and the title of his paper and places at the disposal of the author a definite portion of its program time. Therefore the Society feels that papers thus presented become a definite part of its transactions, the printing of which is essentially a function of the Society.

Under this conviction the Council at its Buffalo meeting unanimously adopted the following resolution:

> *Resolved*, The Society reserves the right of original publication in its official journals of all papers appearing on the programs of its general meetings, divisions, and local sections. The editors are requested to inform authors promptly of decision regarding publication of such papers. This decision can be facilitated by authors sending duplicate copies of their papers in advance to the editor of that journal in which publication is desired.
>
> The Secretary is requested to give proper notice of this action by printing this resolution on the preliminary and final programs of all general meetings.

In justice to authors it is required that the editors give prompt notification as to acceptance of papers for publication or their release. This will be done as speedily as is consistent with careful consideration by the reviewers.

The official ruling is reasonable from every viewpoint and we are confident needs only to be understood to enlist the hearty compliance of every contributor to the program.

THE UNITED STATES' SEARCH FOR NATURAL DEPOSITS OF SOLUBLE POTASH

By H. D. Ruhm

136 Liberty St., New York, N Y.

One of the most widespread elements in the earth's crust is sodium, largely in the form of chloride or common salt, yet very little of this is taken up by plant growth. Associated with sodium in the rocks of the earth, potassium is almost always found in lesser amount, and, strange to say, almost every known vegetable fiber contains appreciable quantities of this metal.

As the earth's entire crust is continually being dissolved and eroded by the waters of the earth, and as "all the rivers run into the sea," sea water is salty, and that saltiness is made up largely of sodium compounds, with some magnesium, calcium, and potassium salts, both sulfates and chlorides.

The Encyclopedia Britannica gives in its early and recent editions the following results of study by Usiglio on the spontaneous evaporation of sea water:

> Up to the time that the water becomes concentrated to specific gravity 1.218, only 0.150 of deposit had formed and that chiefly composed of lime and iron, but between specific gravity 1.218 and 1.313 there is deposited a mixture of
>
> | | Per cent |
> |---|---|
> | Calcium sulfate | 0.0283 |
> | Magnesium sulfate | 0.0624 |
> | Magnesium chloride | 0.0153 |
> | Sodium chloride | 2.7107 |
> | Sodium bromide | 0.0222 |
> | Total | 2.8389 |
>
> Of this we see that about 96 per cent is sodium chloride. Up to this point the separation of the salts has taken place in a fairly regular manner, but now the temperature begins to exert an influence, and some of the salts deposited in the cold of the night dissolve again partially in the heat of the day. By night the liquor gives nearly pure magnesium sulfate; in the day the same sulfate mixed with sodium and potassium chloride is deposited.
>
> The mother liquor now falls a little in density to a specific gravity of 1.3082 to 1.2965, and yields a very mixed deposit of magnesium bromide and chloride, potassium chloride, and magnesium sulfate, with the double magnesium and potassium sulfate, corresponding to the kainite of Stassfurt (Germany). There is also deposited a double magnesium and potassium chloride, similar to the carnallite of Stassfurt, and finally the mother liquor, which has now risen to specific gravity 1.3374, contains only pure magnesium chloride.

It will be readily accepted as indisputable that practically all the deposits of rock salt scattered through the earth's crust have come there as the result of such spontaneous evaporation of ancient seas or lakes.

It will be seen, therefore, that within the layer or bed of purest sodium salt, not even a trace of potash will be found, whereas, in the impure or low-grade rock-salt beds or layers, we may look for lenticular deposits or inclusions of carnallite or kainite, as are found at Stassfurt.

STASSFURT DEPOSITS

Rock salt has been mined from such underground layers or beds in the older portions of Europe for the greater part of a thousand years. Naturally so far as possible the mining was confined to the purest deposits of rock salt, but in the workings at the different levels of the mines there were frequently encountered lenticular masses of low-grade, varicolored, impure salt which, whenever possible, was not disturbed, and was discarded when necessarily mined to get it out of the way. This was known for many years in the rather intensive development of the Stassfurt salt mines by the term "bittersalz" and "abraum-salz," and in the salt-mining district huge piles of this material accumulated.

When Liebig developed the theory of potassium being one of the essential elements of plant food and at the same time discovered that these waste heaps contained considerable percentage of potassium, the potash business of Germany started with the treatment of these piles of "abraum-salz" near Stassfurt for the recovery of the potash content.

The systematic nature of German records enables us to understand easily how the operators of the Stassfurt mine could go back and locate the levels, cross cuts, and stopes where the "abraum-salz" had been most in the way, and this formerly waste and detrimental deposit was eagerly mined for the potash value, coming more and more into demand as Germany's intensive cultivation of her soil proceeded more and more along lines of scientific fertilization.

Whenever Germany has developed a good thing it has not been her custom to help all the other nations to develop the same thing at home, but rather to develop in all other nations the demand for that good thing produced or made in Germany. Proceeding along this line, Germany has conducted for many years the most vigorous propaganda for the introduction into and use by all other countries of her wonderful potash salts for fertilizing and other chemical needs.

Why anyone should think that German potash interests would seriously help to find similar potash deposits in other countries is beyond me to imagine. For years the German scientists have rung the changes on the peculiar geological formation of the Stassfurt deposits so entirely different from the geology of all other known salt deposits that unfortunately only in that geology could the natural deposits of soluble potash be found.

SEARCH FOR OTHER DEPOSITS IN GERMANY

All this time efforts were being made to develop similar deposits of "abraum-salz" in the rock-salt measures known to exist more or less widely through the entire old sea basin of western Prussia and eastern Hanover, and on down into Alsace-Lorraine. The chief potash mines, however, continued to be at Stassfurt where the location of the lenticular deposits

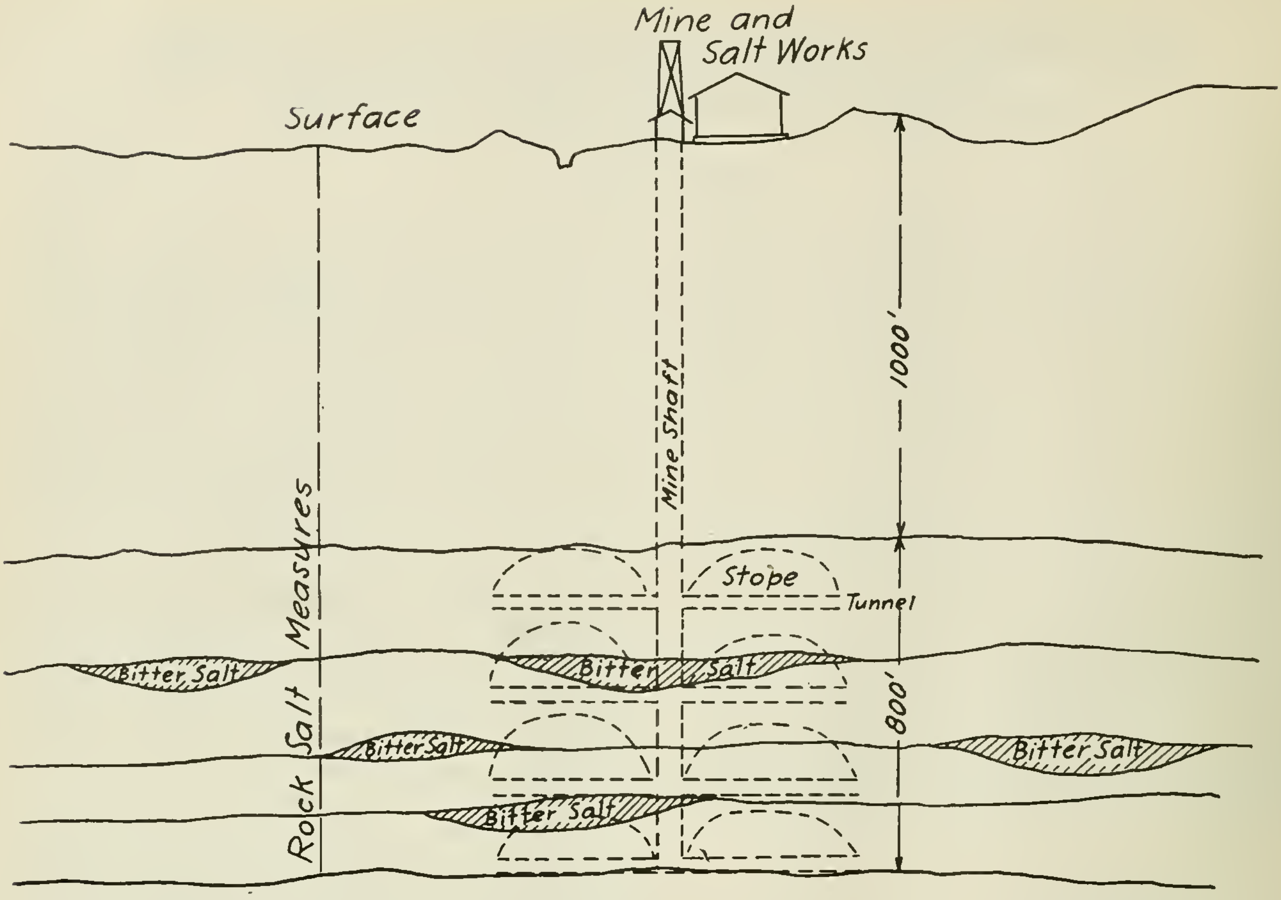

Fig. 1

was known from the records of many years of shaft, level, and stope mining.

With churn drills holes could be put down and the salt measures penetrated, but only with extreme difficulty were the potash deposits discovered; in some holes they got nothing, and in others so slight a trace of potash as not to be worth developing.

After reaching the salt measures with the churn drill, solid cores of the salt strata were taken out by using a core or diamond drill. As is well known, this is accomplished by rotating a shaft on the lower end of which is a pipe or hollow shaft with diamonds or other cutting points set in the bottom end. Water is continually pumped into the hole thus made to counteract the heat of friction, and when the seam or stratum is cut through a solid core of the material is brought out.

Unfortunately, the greater solubility of potash, as compared with soda, created a situation whereby when potash layers were struck, like Huck Finn's apple, "there wasn't no core."

When the discoverer and developer of Aschersleben's enormous deposits thought out the method of using a saturated brine for the liquid in the core drills, instead of fresh water, the real development and extension of the German potash deposits became a possibility as then the potash core came out unaffected; and discoveries multiplied by leaps and bounds until something more than a hundred mines were opened, and only the strong hand of government monopoly by pro-rata allotment of permitted production kept the price up on the fictitious plane maintained.

It is well to note here that, even though prospecting in a salt field absolutely known to contain potash, if the German prospector finds potash in one hole out of three which he puts down, he is fortunate indeed.

I have attempted to illustrate in Fig. 1 a section of an old salt mine such as might have existed at Stassfurt, where the shaft was sunk through the measures, and tunnels run off at different levels, and the salt stoped out and taken to the shaft. The shaded lenses indicate the deposits of "abraum-salz" encountered. Where necessity demanded its removal, it also was brought to the surface and dumped on the waste pile.

In Fig. 2 I have tried to give as well as I could from memory the drawing hanging on the wall of one of the large potash companies, showing a section of the deposits of potash salts being worked by them at the time I was there.

The six borings shown were first made only to a depth indicated by the point D, and of the six only two developed potash. Later deeper drilling to depth E developed one more large deposit to which mine workings had been extended in 1913, and drilling to point F developed two more. It is interesting to note that had 3 and 6 been the only ones put down no potash at all would have been developed.

SEARCH FOR SIMILAR DEPOSITS IN THE UNITED STATES

The efforts to locate potash in this country have been almost entirely confined to searches in the extreme

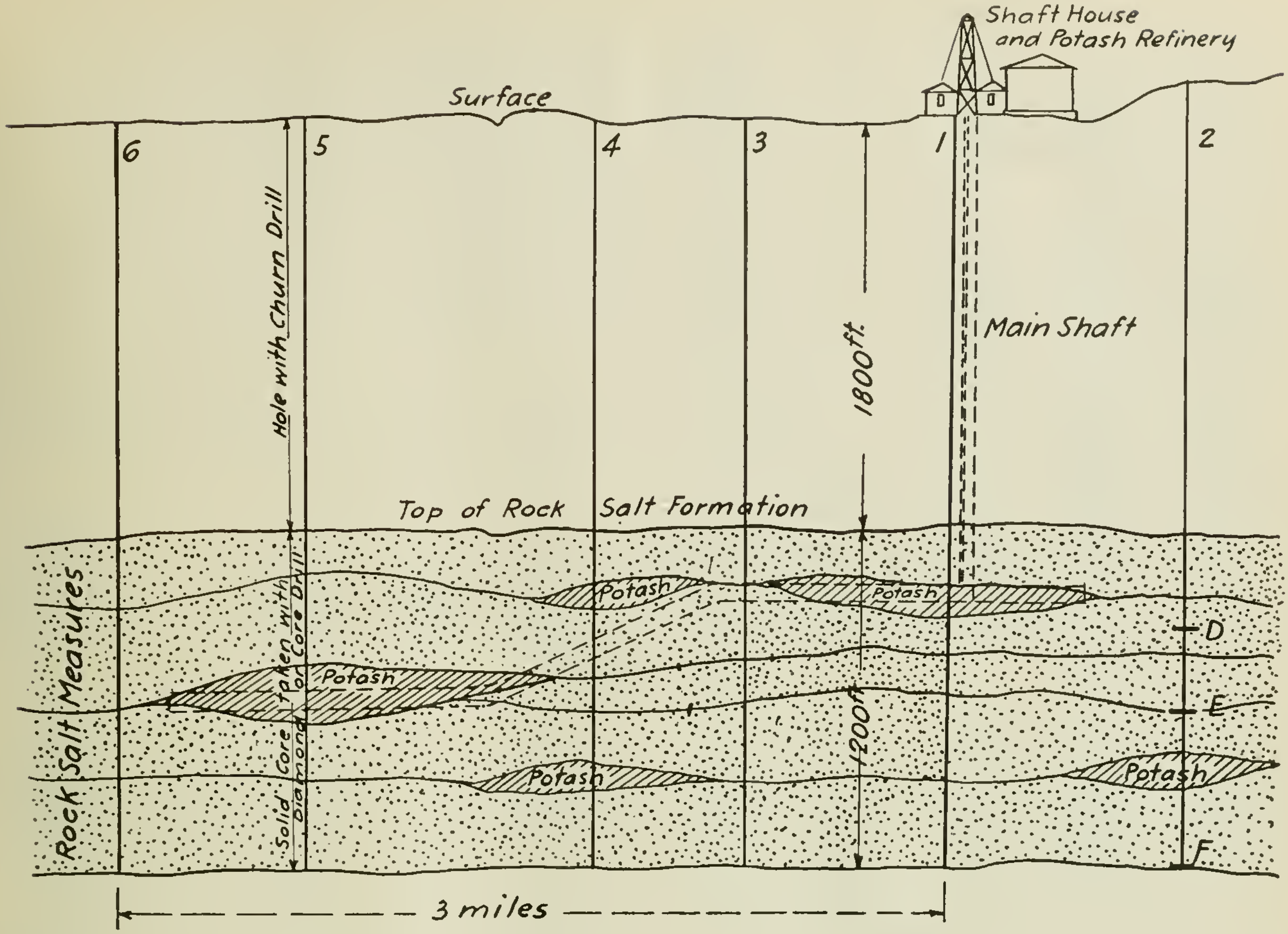

FIG. 2

West where, under normal conditions. the high freight rate to the eastern market would still leave European potash in position to supply to advantage 90 per cent of the demand in this country.

The examination of the New York, Ohio, and Michigan salt fields in this country has been confined to the testing of brines from the various wells, and no core drilling has been done, so far as I am able to learn from public records. The one lot of core drilling of which I am advised was done by private interests with fresh water and naturally no encouraging results were obtained.

The general conclusion seems to have been that only salt deposits of the same geological age as the Stassfurt deposits can contain potash, notwithstanding the very plain evidence from Usiglio's observations that given right conditions, the desiccation of any sea will give similar deposits, and they are likely to exist in any salt beds of considerable thickness.

In comparison with the painstaking and expensive prospecting which was necessary to locate the German deposits even after actual knowledge of their existence had been given by the old workings in salt mines, it is perfectly justifiable to say that the United States has not so far even looked for potash where it would be of real benefit, *i. e.*, in the New York, Ohio, and Michigan salt fields. It is plainly evident that instead of spending enormous sums to investigate far western deposits the Government should spend at least an equal amount in core drilling in the East.

It is of necessity a government task to develop this matter regardless of the fact that any work done will be on private instead of government land. I say this for the reason that whenever the presence of potash deposits in the salt fields is definitely proved, the price of potash will drop on account of the fierce competition which will immediately spring up, until there will be no more profit in producing potash than in producing common salt. The benefit that will accrue to the farmer of the United States, however, will be incalculable.

So long as it remains necessary for private initiative to develop this problem, no one will be found willing to incur the enormous expense under the certainty that his business will be immediately shorn of its profitable nature when his neighbor takes advantage of his discovery.

For comparison with the general statement now so confidently made that "the salt deposits of the eastern states contain no potash of moment, as is shown by the investigation and analysis of all the samples of brines gathered from all the wells and drillings available, in only a few of which is found even a slight showing of potash," it is well to note the following quotation from Encyclopedia Britannica, reprint edition of 1894:

The deposits of salt in the United States are unimportant.

The country possesses no really considerable salt industry but is supplied so far as interior consumption is concerned to a small extent by brine springs.

The principal supplies, however, are derived from England, and the shores of Spain and Portugal. The same remark applies to Canada.

This statement was probably made about 1860 to 1870 and was doubtless true then, but in 1887 the United States produced over 1,100,000 tons; in 1900, 2,800,000; and in 1913, 4,800,000 tons. Likewise the price of common salt in 1866 was about $13.00 per ton, and in 1887, $3.50 per ton at the mines, while in 1913 it got as low as $2.00 per ton.

When the potash deposits which are surely there are developed, $5 or $10 per ton for 80 per cent muriate of potash will be a high price, and no greater benefit can accrue to the farmer than this.

If the Geological Survey and the Agricultural Department will make the search they will earn the everlasting gratitude of the farmer, and release the stranglehold which European potash has on this country.

Pending that time, the only hope for normally priced potash is for the final successful development of the processes for recovering potash from greensand or feldspar, one very large plant for which is nearing completion in New Jersey, which will produce potash of the highest grades of all salts required. By the sale of its valuable by-product at ordinary prices its potash cost will be less than nothing.

The Government's potash search reminds me of the golfer who, after losing the hole, looking for his ball in the heavy "rough" where his unscrupulous opponent "thought it went," finds it too late nicely placed in the fair green where "there was no use looking as it couldn't have come that far."

OUR FOREIGN TRADE IN CHEMICALS

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Two years of peace have not weakened the commanding position in foreign trade attained during the war by the American chemical industry. Official statistics for the fiscal year 1920 demonstrate that this country has been able to keep its trade in chemical and allied products very near the high mark set during the war, despite the loss of markets for purely war supplies, and despite the pressing demands that must be met in the domestic market

In almost all lines, except munitions, the exports in 1920 exceeded in value those in 1918, a fact that can be explained in some cases, perhaps, by rising prices, but which nevertheless warrants the assertion that the position has not been weakened. These exports, which very greatly exceed those of the last normal pre-war year, are made up almost entirely of manufactured products.

Imports have more than held their own and comprise raw and partly manufactured products required for further advancement by American chemical manufacturers.

A very rough estimate puts the total value of exports of all chemical and allied products at a billion and a quarter dollars in 1920, a slight increase over the total for 1918, and about four times the figure for 1914, the last normal year. Imports, estimated in the same rough way, were valued at more than a billion and a half dollars in 1920, an increase of some 80 per cent over 1918, and nearly four times the total for 1914. Both exports and imports have quadrupled since 1914 Sugar is included in these totals and accounts for much of the increase in imports.

Although values are no longer a reliable guide in making trade comparisons, a summary table of values has been compiled to show at a glance the tendencies in the chemical trade for the fiscal years ended June 30, 1914, 1918, and 1920; that is, the last normal year, a full year of America's participation in the war, and the year just closed. Apology is offered for the groupings in this table, and also for the fact that 1918 has been selected in preference to any one of several others. It is, of course, impossible to arrive at such totals for quantities, but in the more detailed tables that follow, quantities have been given wherever possible, values being stated only when quantities were not available. All compilations are based upon statistics of the Bureau of Foreign and Domestic Commerce, Washington, D. C.

SUMMARY OF FOREIGN TRADE IN CHEMICALS AND ALLIED PRODUCTS
(In Millions of Dollars)

	IMPORTS			EXPORTS		
CLASSES	1914	1918	1920	1914	1918	1920
Chemicals	72	109	85	15	140	92
Drugs, medicines, etc	9	11	20	11	21	41
Dyes, dyewoods	10	9	6	([2])	17	26
Explosives	1	8	2	6	379	28
Fertilizers	28	5	39	12	6	33
Gums, resins, etc	88	227	330	20	11	37
Oils, fats, waxes	75	199	319	194	367	607
Paints, pigments, etc	2	1	2	7	17	27
Tanning materials	5	7	12	1	4	6
Paper and pulp	30	66	106	6	30	33
Miscellaneous products[1]	120	253	701	44	132	324
Miscellaneous materials	8	6	9	2	3	4
TOTAL	448	901	1631	318	1127	1258

[1] The importance of this class is due to the inclusion of sugar. The articles making up this class are shown in the detailed table of miscellaneous products.

[2] $400,000.

THE TRADE IN CHEMICALS[1]

There has been a falling off in the value of both exports and imports of chemicals since the war, but the decline is due almost solely to the cessation of the demand for war supplies. Exports of picric acid, for instance, have practically ceased, and this was an item of prime importance in the total for the war year 1918. Aside from war supplies, the statistics indicate that the exports of chemicals have as a whole been maintained since hostilities ceased, and have for some groups been increased. Sodas have more than held their own, owing largely to the insatiable demand for caustic soda the world over. The war stimulated the growth of domestic industries in all countries, and many of these industries require caustic soda. The 230,000,000 lbs. of this alkali exported in 1920 represent an increase of more than 70 per cent over the quantity shipped in 1918, while the foreign sales in 1914 were not important enough to be stated separately in the official statistics. In a few cases, such as calcium carbide and acetate of lime, the 1920 figures are lower than in 1914, but for the class as a whole the trade is greatly in excess of the pre-war totals, as will be seen in the table entitled "Trade in Chemicals, Drugs, Dyes, etc."

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[1] The term "chemicals" is here used in the usual restricted sense, as not including drugs, medicines, and dyes.

Imports have fallen off as compared in value with those of 1918, but considering the rise in prices, the total is probably about the same as in 1914.

TRADE IN CHEMICALS, DRUGS, DYES, ETC.

ARTICLES	1914	1918	1920
Imports			
Acids (except coal-tar acids):			
Oxalic, lbs.	8,507,850	792,383	1,401,547
All other, value	$1,133,252	$3,051,634	$4,004,018
Albumin, egg, lbs.	(1)	(1)	8,956,845
Ammonia, muriate, lbs.	9,176,729	1,120,074	5,344,028
Argols, lbs.	29,793,911	30,267,388	26,638,337
Arsenic or orpiment, lbs.	4,432,793	9,260,768	6,470,700
Balsams, not containing alcohol, lbs.	(1)	(1)	745,151
Calcium, acetate, crude chloride, carbide and nitrate, lbs.	(1)	(1)	76,845,476
Chemical and medicinal compounds, n. e. s.:			
Alkalies, alkaloids, preparations, mixtures, etc., lbs.	(1)	(1)	6,907,035
Medicinal preparations (see also coal-tar products), value	$1,031,054	$519,338	$5,625,586
All other	(1)	(1)	$1,388,577
Cinchona bark, and alkaloids or salts of:			
Barks, cinchona, or other from which quinine may be extracted, lbs.	3,648,868	3,273,628	5,242,724
Quinine, sulfate of, and all alkaloids or salts of cinchona bark, oz.	2,879,466	1,445,702	4,580,807
Coal-tar products:			
Crudes			
Acid, carbolic, lbs.	8,392,995	127,574	157,319
Benzol, lbs.	(1)	(1)	170,519
Cresol, lbs.	(1)	(1)	8,188,303
Creosote oil, gal.	60,900,435	3,857,869	8,338,761
Naphthalene, lbs.	(1)	(1)	6,113,858
Tar and pitch, bbls.	(1)	25,540	20,607
Toluol, lbs.	(1)	(1)	1,195,706
All other crudes, value	(1)	(1)	$65,818
Intermediates			
Acids			
Carbolic (phenol), lbs.	(1)	498,264	30
All other, lbs.	(1)	(1)	11,512
Aniline salts, lbs.	3,184,467	21,273	....
All other intermediates	(1)	(1)	$217,653
Finished products			
Alizarin and dyes, lbs.	2,633,414	29,323	257,841
Colors or dyes, n. e. s., value	$7,241,406	$2,507,296	$3,775,216
Indigo, synthetic, lbs.	8,125,211[2]	1,012,585	1,014,100
Medicinal preparations	(1)	(1)	$112,611
Other finished products	(1)	(1)	$79,216
All other coal-tar products, value	$1,636,750	$520,941	....
Extracts and decoctions for dyeing, lbs.	(1)	(1)	1,581,534
Extracts for tanning:			
Quebracho, lbs.	93,329,087	101,523,282	154,944,717
All other, lbs.	8,710,040	4,573,925	7,380,920
Fusel oil and butyl alcohol, lbs.	5,802,369	1,606,528	6,196,179
Glycerol, crude, lbs.	36,409,619	1,875,531	15,656,463
Indigo, natural, lbs.	(1)	2,113,912	126,539
Iodine, lbs.	195,087	268,281	523,313
Lactarene, lbs.	10,798,614	12,133,855	24,039,313
Licorice root, lbs.	115,636,131	26,982,932	48,045,373
Lime, chloride of, lbs.	47,423,651	4,285	830,207
Citrate of, lbs.	3,097,265	4,253,686	10,431,314
Magnesite, not purified, tons	289,494,316	23,499,789	27,503
Opium, containing 9 per cent or more morphine, lbs.	455,200	157,834	628,979
Perfumeries, cosmetics, etc., value	$2,309,027	$3,497,695	$5,545,606
Potash (not for fertilizer):			
Carbonate, lbs.	20,603,593	14,468,211	22,142,554
Cyanide, lbs.	808,721	144,225	5,175,608
Hydrate, not over 15 per cent caustic soda, lbs.	8,450,402	11,732	782,477
Nitrate, lbs.	3,546,580	8,820,367	26,862,012
All other, lbs.	5,775,588	1,662,153	2,198,178

[1] Not stated separately.

[2] Stated as "Indigo, natural or synthetic" in 1914, but was probably largely synthetic.

CHEMICALS, DRUGS, DYES, ETC. (*Concluded*)

ARTICLES	1914	1918	1920
Imports			
Soda:			
Cyanide, lbs.	(1)	84,652	8,629,502
Nitrate, tons	564,049	1,607,020	907,041
All other salts of, value	$487,038	$389,384	$1,642,589
Sulfur, tons	19,389	282	47
Sumac, lbs.	10,770,340	14,046,662	21,180,414
All other chemicals, drugs, dyes, etc., value	$13,676,032	$18,881,465	$6,727,411
Exports			
Acids:			
Carbolic, lbs.	(1)	8,688,554	2,223,205
Nitric, lbs.	(1)	961,494	820,517
Picric, lbs.	(1)	56,193,952	8,073
Sulfuric, lbs.	12,131,750	67,654,722	32,336,893
All other, value	$357,035	$5,673,707	$5,291,987
Alcohol, wood, gal.	1,598,776	2,538,001	687,008
Calcium carbide, lbs.	32,845,649	28,869,686	21,164,404
Coal tar, bbls.	22,150	53,955	81,640
Coal-tar distillates, n. e. s.:			
Benzol, lbs.	(1)	25,400,852	17,282,368
All other, value	(1)	$5,620,851	$3,611,514
Copper sulfate, lbs.	7,375,775	15,164,078	4,511,724
Dyes and dyestuffs:			
Aniline dyes, value	(1)	$7,298,298	$17,130,397
Logwood extract, value	(1)	$2,339,480	$1,832,231
All other, value	$356,919[2]	$7,284,110	$6,829,937
Extracts for tanning, value	$639,941	$3,804,563	$6,016,438
Formaldehyde, value	(1)	$866,038	$2,289,217
Glycerol, lbs.	36,409,619	1,875,531	2,257,623
Infants' food, value	(1)	$1,908,141	$3,032,330
Lime, acetate of, lbs.	68,160,224	15,490,032	32,885,132
Chloride of, lbs.	(1)	13,060,401	31,252,379
Medicinal and pharmaceutical preparations, value	$6,721,978	$10,190,188	$20,118,271
Perfumery and cosmetics, value	$2,309,027	$3,965,465	$7,979,237
Petroleum jelly, value	$661,889	$1,278,658	$3,156,286
Potash:			
Chlorate, lbs.	(1)	1,564,662	2,845,858
All other, value	(1)	$961,989	$3,362,827
Roots, herbs, barks:			
Ginseng, lbs.	224,605	259,892	220,970
All other, value	$513,071	$784,514	$1,793,064
Soda:			
Bicarbonate, lbs.	(1)	(1)	11,998,510[3]
Borax, lbs.	(1)	(1)	10,943,110[3]
Caustic, lbs.	(1)	134,729,691	229,684,163
Sal soda, lbs.	(1)	14,076,264	12,763,399
Silicate, lbs.	(1)	26,127,870	33,692,535
Ash, lbs.	(1)	198,902,457	115,997,980
All other salts of, value	(1)	$7,421,521	$7,471,808
Sulfur, tons	110,022	140,525	393,404
All other chemicals, etc., value	$9,019,582	$42,945,083	$42,573,500

[1] Not shown separately.

[2] Represents the total value of all dyes and dyestuffs in 1914.

[3] Period from Jan. 1 to June 30, 1920.

DRUGS, MEDICINES, AND TOILET PREPARATIONS

Both exports and imports of this class of chemicals have increased in value at a rather remarkable rate since 1918. Increases in prices have not been sufficient to account for this fact. Exports of medicinal and pharmaceutical preparations alone were valued at $20,000,000 in 1920, or twice the total for 1918 and about three times the total for 1914. A good part of the new business is with districts that once depended pretty largely upon Europe for such supplies. While the exports have been manufactured products, the imports are almost entirely raw materials, the largest item being cinchona bark and products, the quantity of which has doubled since 1918, a year somewhat below the 1914 normal. (See table "Trade in Chemicals, Drugs, Dyes, etc.")

DYES

We are nearly two years away from the armistice, yet the German avalanche of dyes has not overwhelmed us—a circumstance attributed in some quarters to the fact that we have had "more luck than sense." The protection asked for at home has been withheld, but outside circumstances have postponed the crisis. Statistics show that the value of imported dyes, dyestuffs, and dyewoods of all kinds has decreased since 1918, but the quantity of synthetic dyes has increased somewhat, the bulk of the supplies still coming from Switzerland. The imports of natural dyes and raw materials have fallen away as the domestic industry developed. In the meantime, our exports of aniline dyes have more than doubled, reaching a value of $17,000,000 in 1920, while our sales of logwood extract and all other dyes have shown a slight falling off. A year or so ago Japan was the principal purchaser of our synthetic colors, but the largest shipments now go to China and India, where the textile industry is developing rapidly. All in all, it is conservative to say that the dye industry in this country has been developed more successfully than in any of the other countries that were thrown upon their own resources in 1914. Details of the dye trade are shown in the table "Trade in Chemicals, Drugs, Dyes, etc.," and the dyewoods are mentioned in the table "Trade in Miscellaneous Materials."

TANNING MATERIALS

Imports of tanning extracts were 50 per cent higher in quantity in 1920 than in 1918 and 1914, quebracho extract being the big item, with a total of 155,000,000 lbs. Purchases of bark and wood are falling off as the countries of origin learn to manufacture the extract. Exports of tanning extracts have also increased, the total value in 1920 being about $6,000,000, as compared with $3,800,000 in 1918, and less than a million dollars in 1914. The value of exports is still below that of imports. (See table "Trade in Chemicals, Drugs, Dyes, etc.," for extracts, and "Trade in Miscellaneous Materials" for bark and wood.)

OILS, FATS, AND WAXES

There have been some sensational developments in our trade in vegetable oils. The imports of soy-bean oil, which in 1914 totaled only a little over 16,000,000 lbs., reached the remarkable figure of 337,000,000 lbs. during the war year 1918, only to fall back to 196,000,000 lbs. in 1920. It is probable that disturbed conditions in northeastern China had something to do with the decline. Coconut oil again leads all the vegetable oils in quantity, with a total of 269,000,000 lbs. in 1920, a gain of 10,000,000 lbs. over 1918, and of nearly 200,000,000 lbs. over 1914. In fact, coconut oil was exported from this country to the extent of 141,000,000 lbs. in 1920, its first appearance in official export statistics. Another newcomer among the exports is cocoa butter, with a total of more than 11,000,000 lbs. But the most interesting is soy-bean oil, which was exported to the extent of about 68,000,000 lbs., in spite of the falling off in imports. As the total of "all other" vegetable oils in 1918 was less than $4,000,000, or about the same as in 1920, it is evident that this new export business has come into existence since the end of the war.

Of the mineral oils, the export of fuel and gas oil is only about half of the total of more than a billion gallons in 1918, although still higher than in 1914. Shipments of illuminating oil have, on the other hand, increased more than 70 per cent since 1918, although the total is still below the billion and more gallons for 1914. Exports of lubricating oil have increased steadily, as have those of gasoline.

A summary table showing the trade in oils by value follows:

SUMMARY OF TRADE IN OILS

Articles	1914	1918	1920
Imports			
Oils:			
Animal	$1,034,000	$3,678,000	$3,629,000
Mineral	13,666,000	21,926,000	41,050,000
Fixed vegetable	28,829,000	87,986,000	141,023,000
Essential	3,492,000	4,338,000	90,439,000
Oil-bearing materials:			
Castor beans	1,139,000	2,274,000	30,674,000
Copra	2,395,000	26,946,000	14,971,000
Flaxseed	10,571,000	34,217,000	76,845,000
Peanuts	1,899,000	4,771,000	12,382,000
Exports			
Oils:			
Animal	822,000	1,155,000	3,426,000
Mineral	152,174,000	289,037,000	426,598,000
Fixed vegetable	15,624,000	23,930,000	96,226,000
Essential	628,000	1,091,000	2,230,000

Details of the oil trade are shown in the next table:

TRADE IN OILS, FATS, AND WAXES

Articles	1914	1918	1920
Imports			
Oils, animal:			
Cod and codliver, gal	1,393,706[1]	2,021,656	1,943,357
All other, gal	1,488,973	2,906,473	1,294,134
Oils, mineral:			
Crude, gal	773,052,480	1,347,543,144	2,826,860,902
Refined			
Benzene, gasoline, naphtha, gal	16,139,912	11,069,899	22,037,592
All other, gal	1,945,007	45,114,581	59,851,312
Oils, fixed vegetable:			
Chinese nut, gal	4,932,444	4,815,740	10,613,638
Cocoa butter or butterine, lbs.	2,838,761	405	41,500
Coconut, lbs	74,386,213	259,194,853	269,226,966
Cottonseed, lbs	17,293,201	14,291,313	24,164,821
Linseed, gal	192,282	50,827	4,550,391
Olive, non-edible, gal	763,924	114,324	216,145
Olive, edible, gal	6,217,560	2,537,512	6,812,596
Palm, lbs	58,040,202	27,405,231	50,163,387
Palm-kernel, lbs	34,327,600	18,618	53,508
Peanut, gal	1,337,136	8,288,756	22,064,363
Rape-seed, gal	1,464,265	3,056,438	1,229,526
Soy-bean, lbs	16,362,452	336,824,646	195,773,594
All other, value	$439,009	$2,027,137	$2,974,966
Oils, distilled and essential:			
Birch tar and cajeput, value.	(2)	$25,981	$20,019
Lemon, lbs	385,959	628,057	870,170
All other, value	$2,633,789	$3,884,287	$8,370,317
Oleostearin, lbs	5,243,553	6,575,379	1,307,837
Paraffin (except oil), lbs	7,495,459	8,997,023	8,687,728
Wax:			
Beeswax, lbs	1,412,200	1,826,618	3,923,687
Mineral, lbs	8,086,422	1,708,514	2,816,700
Vegetable, lbs	4,255,686	8,707,396	9,949,567
Grease and oils, n. e. s., lbs	22,322,492	28,000,428	42,165,287
Oil seeds and nuts:			
Castor beans, bu	1,030,543	1,222,934	1,416,328
Coconuts in shell, value	$2,133,416	$2,788,635	$4,830,548
Copra, lbs	45,437,155	486,996,112	218,521,946
Flaxseed, bu	8,653,235	13,187,609	23,391,934
Peanuts			
Not shelled, lbs	17,472,631	3,150,747	12,067,998
Shelled, lbs	27,077,158	73,362,215	120,344,425
Exports			
Oils, animal:			
Fish, gal	448,366	464,936	1,310,478
Lard, gal	110,199	91,585	130,635
All other, gal	891,035	442,496	1,452,489
Oils, mineral:			
Crude, gal	146,477,342	186,672,778	354,357,795
Refined or manufactured			
Fuel and gas, gal	475,143,205	1,224,807,405	690,895,418
Illuminating, gal	1,157,283,310	528,805,501	914,137,071
Lubricating, gal	196,884,696	269,667,145	339,701,134
Gasoline, gal	151,611,537	260,300,337	294,949,121
Other naphthas, gal	40,840,730	207,905,009	185,265,961
Residuum, gal	113,370,245	1,879,475	48,300,361
Oils, fixed vegetable:			
Cocoa butter, lbs	(2)	(2)	11,048,416
Coconut oil, lbs	(2)	(2)	141,063,943
Corn, lbs	18,281,576	1,831,114	12,482,679
Cottonseed, lbs	192,963,079	100,005,074	159,400,618
Linseed, gal	239,198	1,187,850	1,136,585
Peanut, lbs	(2)	(2)	4,922,781
Soy-bean, lbs	(2)	(2)	67,781,974
All other, value	$338,956	$3,948,483	$3,258,446
Oils, distilled and essential:			
Peppermint, lbs	117,809	76,247	90,255
All other, value	$230,557	$857,044	$1,551,992
Grease:			
Lubricating, value	$2,394,918	$2,986,815	$6,157,323
Soap stock, etc., value	$5,046,959	$2,612,488	$8,994,603
Oleo oil, lbs	97,017,065	56,648,102	74,529,394
Oleomargarine, lbs	2,532,821	6,404,896	20,952,180
Paraffin:			
Unrefined, lbs	186,357,728	84,657,140	79,023,341
Refined, lbs	(2)	162,003,480	81,784,255
Stearin:			
Animal, lbs	2,724,182	10,252,522	22,505,602
Vegetable, lbs	(2)	1,293,327	5,138,225
Wax:			
Beeswax, lbs	96,215	189,871	641,357
Manufactures of, value	$112,193	$717,181	$1,203,471
Oil seeds and nuts:			
Cottonseed, lbs	16,342,384	1,565,052	3,505,118
Flaxseed, bu	305,546	21,481	24,044
Peanuts, lbs.	8,054,817	12,488,209	14,137,956

[1] Period from Oct. 3, 1913, to June 30, 1914.

[2] Not stated separately.

GUMS, RESINS, AND NAVAL STORES

Substantial increases are shown in the imports of nearly all the gums and resins as compared with the figures for 1918 and 1914. The total of 34,000,000 lbs. of shellac is twice that for 1914, while the 44,000,000 lbs. of copal, kauri, and damar is nearly 10,000,000 lbs. in excess of that for the last normal year. The increase in purchases of rubber has been enormous, as the total of 632,000,000 lbs. in 1920 is nearly five times the amount brought in in 1914, and almost double that recorded in 1918.

The exports of naval stores are still far below the 1914 total in quantity, although an improvement is shown over 1918. Detailed figures follow:

Trade in Gums, Resins, and Naval Stores

Articles	1914	1918	1920
Imports			
Camphor:			
Crude, natural, lbs.	3,476,908	3,638,384	4,025,517
Refined and synthetic, lbs.	566,106	1,189,932	1,685,633
Chicle, lbs.	8,040,891	6,408,093	9,699,863
Copal, kauri, damar, lbs.	32,693,412	30,003,549	44,480,003
Gambier, lbs.	14,936.129	8,964,832	10,207,013
Gum arabic, lbs.	(1)	(1)	66,718,308
Shellac, lbs.	16,719,756	22,913,256	34,151,209
Other gums, lbs.	....	2,622,098	14,641,434
India rubber, etc.:			
Balata, lbs.	1,533,024	2,449,881	2,013,737
Guayule gum, lbs.	1,475,804	4,307,539	1,314,913
Gutta joolatong, lbs.	24,926,571	17,475,863	18,392,164
Gutta-percha, lbs.	1,846,109	1,151,312	6,496,309
India rubber, lbs.	131,995,742	389,599,015	632,392,636
India-rubber scrap, lbs.	25,958,261	13,980,303	14,236,098
Exports			
Naval stores:			
Rosin, bbls.	2 417,950	1,073,889	1,321,535
Tar, turpentine, pitch, bbls.	351,352	82,030	61,826
Turpentine, spirits of, gal.	18,900,704	5,100,124	7,461,455

[1] Not stated separately.

FERTILIZERS

Potash and manure salts, which were practically non-existent in the import statistics in 1918, came over in considerable quantities in 1920, so that something like half of the total for 1914 was attained. There is no telling what the total would have been if there had been no obstacles in the way of getting supplies. Accumulated demands abroad for our phosphates, on the other hand, brought the export total much above the 1914 figure. The exports of 93,000 tons of superphosphates are an interesting item. The total in 1918 was only 6,155 tons, and there was no note made of this product in 1914. Details are given in the following table, which does not, however, include sodium nitrate:

Trade in Fertilizers

Articles	1914	1918	1920
Imports			
Ammonium sulfate, tons	83,377	3,983	2,587
Bone dust, ash, and meal, tons	41,450	8,511	7,340
Calcium cyanamide, tons	(1)	(1)	84,678
Guano, tons	21,887	10,096	18,796
Kainite, tons	541,846	....	274,761
Manure salts, tons	261,342	190	249,348
Potash, n. e. s.:			
Muriate, tons	237,886	723	110,324
Sulfate, tons	45,139	135	6,356
All other substances used only as fertilizers, value	$6,199,554	$4,089,989	$4,757,066
Exports			
Phosphate rock:			
High-grade pebble rock, tons	475,335	25,652	351,352
Land pebble, tons	1,000,630	110,909	395,581
All other, tons	1,906	25,798	30,348
Superphosphates, tons	(1)	6,155	93,432
Ammonium sulfate, tons	(1)	(1)	17,489
All other fertilizers, tons	61,601	84,410	239,091

[1] Not stated separately.

ORES AND METALS

Although not included in the summary table at the beginning of the article, it is assumed that the following data on the trade in ores and metals not advanced beyond the bar and ingot stage will be of some little interest to certain branches of the chemical industry.

Summary of Trade in Principal Metals

Articles	1914	1918	1920
Imports			
Antimony	$696,000	$4,435,000	$1,284,000
Chromate of iron	737,000	1,543,000	1,419,000
Copper	54,506,000	122,450,000	94,310,000
Iron	11,879,000	9,652,000	12,221,000
Lead	2,057,000	11,970,000	6,817,000
Manganese	1,841,000	11,945,000	8,086,000
Nickel	6,110,000	9,120,000	6,848,000
Platinum	3,976,000	4,575,000	6,990,000
Tin	39,422,000	84,834,000	92,790,000
Tungsten ore	114,000	5,794,000	2,589,000
Zinc	616,000	2,560,000	965,000
Exports			
Aluminium	1,102,000	8,746,000	5,195,000
Bauxite concentrates	616,000	1,465,000	1,709,000
Copper	149,480,000	244,328,000	127,996,000
Ferrovanadium	503,000	2,578,000	254,000
Iron	6,261,000	20,579,000	14,454,000
Lead	2,610,000	17,376,000	4,207,000
Nickel	9,404,000	7,681,000	1,144,000
Tungsten and ferrotungsten	....	4,056,000	58,000
Zinc	995,000	28,015,000	22,927,000

MISCELLANEOUS MATERIALS

The export and import trade in a number of materials that could not conveniently be grouped elsewhere is shown in the following table:

Trade in Miscellaneous Materials

Articles	1914	1918	1920
Imports			
Asphaltum and bitumen, tons	180,689	139,899	93,397
Blood, dried, value	$391,816	$462,703	$678,307
Bones, hoofs, horns, value	$1,061,466	$1,374,546	$1,754,892
Dyewoods, crude state:			
Logwood, tons	30,062	52,027	45,073
All other, tons	7,663	35,449	3,358
Fish sounds, lbs.	(1)	331,248	79,679
Gelatin, unmanufactured, lbs.	2,341,317	365,586	1,121,117
Hide cuttings and other glue stock, lbs.	2,158,514[2]	21,710,205	26,248,154
Moss and seaweed:			
Crude, value	$301,259	$230,163	$459,912
All other, value	$54,376	$8,514	$40,711
Rennets, value	$129,720	$62,173	$159,039
Salt, 100 lbs.	3,076,071	1,028,231	1,756,240
Tanning materials:			
Mangrove bark, tons	7,689	73,956	2,544
Quebracho wood, tons	73,956	45,440	33,672
All other, value	$468,230	$496,070	$2,757,859
Vanilla beans, lbs.	897,100	914,668	1,130,336
Exports			
Asphaltum:			
Unmanufactured, tons	49,831	22,052	47,024
Manufactures of, value	$362,347	$488,892	$682,753
Barks for tanning, tons	(1)	194	513
Moss, value	$51,006	$99,793	$141,000
Salt, 100 lbs.	1,489,312	2,670,458	2,574,937

[1] Not stated separately.
[2] Quantity not given for 1914.

MISCELLANEOUS PRODUCTS

A number of products usually considered in connection with the chemical industry have been grouped in the next table. The most important of these is sugar, the inclusion of which gives the group a total that is misleading. It should be borne in mind that large quantities of sugar are now purchased in Cuba on British account, to be refined here and then shipped to England. This sugar is included in both the import and export statistics.

While the summary table at the beginning of this article shows that the value of paper and pulp exported has increased since 1918, the following table shows that the quantity has actually decreased, although still greater than in 1914.

The export trade in explosives has been knocked "galley west" by the return of peace, but there seems to be sufficient unpleasantness in some quarters to support a larger business than existed in 1914.

A good growing trade in paints and varnishes will be noted in examining the statistics in this table.

TRADE IN MISCELLANEOUS PRODUCTS

ARTICLES	1914	1918	1920
Imports			
Collodion, and manufactures of, value	$569,763	$53,637	$82,940
Explosives:			
Fulminates, gunpowder, etc., value	$256,379	$7,860,139	$2,369,250
All other, value	$600,958	$437,010	$765,412
Glass and glassware, value	$8,191,833	$1,723,014	$3,582,377
Glue and glue size, lbs.	22,714,877	2,048,543	1,410,104
Matches, value	$882,812	$3,856,961	$1,096,982
Oilcloth for floors:			
Linoleum, sq. yds.	3,724,086	38,584	522,999
Oilcloth, sq. yds.	340,288	5,060	62,372
Paints, pigments, etc., value	$2,325,222	$961,047	$1,975,769
Paper and pulp:			
Printing paper			
Not over 8 c. per lb., lbs.	536,815,288[1]	1,203,762,118[1]	1,322,890,825
All other, lbs.	6,053,429	278,367	1,371,576
Surface-coated paper, lbs.	6,925,505	380,153	....
Wrapping paper, lbs.	36,515,554	6,150,942	4,983,817
Wood pulp			
Mechanical, tons	177,484	189,599	194,119
Chemical, unbleached, tons	302,963	296,465	442,844
Chemical, bleached, tons	88,917	18,044	89,587
Photographic goods:			
Dry plates, value	(2)	$33,857	$25,808
Motion-picture films			
Not exposed, lin. ft.	44,717,323[3]	47,462,715	46,485,424
Negatives, lin. ft.	$402,704[4]	$713,363	$1,417,774
Positives, lin. ft.	$20,057,144	$3,374,497	$3,327,566
Other films and plates, value	$324,535	$203,719	$1,355,832
Soap:			
Castile, lbs.	4,622,082	1,016,399	2,352,974
All other, value	$460,485	$211,149	$192,103
Sugar and molasses:			
Molasses, gals.	51,410,271	130,730,861	154,670,200
Sugar			
Beet, lbs.	2,367,708	750	1,219,834
Cane, lbs.	5,061,564,621	4,898,277,025	7,590,911,767
Exports			
Baking powder, lbs.	2,725,964	6,046,455	5,595,126
Blacking and polishes, value	$649,395	$1,009,100	$2,845,110
Candles, lbs.	3,047,756	6,761,767	7,691,420
Celluloid and manufactures, value	$1,387,541	$3,744,745	$10,044,242
Chewing gum, value	$178,630	$1,896,135	$2,617,483
Explosives:			
Cartridges, loaded, value	$3,521,533	$13,672,371	$9,729,937
Dynamite, lbs.	14,464,601	18,911,668	12,566,057
Fuses, value	(2)	$19,346,554	$709,662
Gunpowder, lbs.	989,385	340,516,883	1,721,991

[1] Valued at not above 5 cents a pound prior to April 24, 1920.
[2] Not stated separately.
[3] From Oct. 3, 1913, to June 30, 1914.
[4] Stated as "All other" motion-picture films in 1914.

TRADE IN MISCELLANEOUS PRODUCTS (*Concluded*)

ARTICLES	1914	1918	1920
Exports			
Explosives (*Continued*):			
Shells and projectiles, loaded, value	(1)	$40,130,298	$12,295,519
All other, value	$916,280	$38,559,249	$2,250,566
Flavoring extracts and fruit juices, value	(1)	$1,018,102	$1,425,380
Glass and glassware, value	$3,729,623	$14,012,656	$25,906,621
Glucose and grape sugar:			
Glucose, lbs.	162,680,378	80,970,744	219,793,235
Grape sugar, lbs.	36,850,496	16,887,557	25,839,015
Glue, lbs.	2,351,770	4,935,250	13,141,294
India-rubber manufactures, value	$12,441,220	$31,675,847	$69,226,716
Ink:			
Printers', value	$443,377	$882,062	$1,590,096
All other, value	$181,697	$407,093	$836,436
Matches, value	$77,736	$471,385	$558,911
Metal polish, value	$162,504	$192,691	$451,934
Mucilage and paste, value	$95,013	$399,295	$654,827
Oilcloth:			
For floors, sq. yds.	163,214	1,259,805	2,623,060
All other, value	$666,479	$1,277,777	$2,475,699
Paints, pigments, etc.:			
Dry colors			
Carbon, bone, and lamp-black, value	$421,548	$1,111,265	$1,959,208
All other, value	$690,836	$1,907,667	$2,991,618
Lead			
Red, lbs.	(1)	4,792,330	3,027,731
White, lbs.	16,845,154	18,235,783	34,441,918
Ready-mixed paints, gal.	852,910	1,521,588	2,553,091
Varnish, gal.	1,069,501	736,949	1,529,592
Zinc oxide, lbs.	29,197,790	25,862,063	30,925,983
All other, value	$1,779,863	$4,875,006	$7,756,076
Paper and pulp:			
Newsprint, lbs.	88,966,738	220,080,301	123,335,408
Other printing paper, lbs.	28,602,134	90,353,235	92,076,860
Wrapping paper, lbs.	14,133,097	59,350,946	65,163,463
Writing paper and envelopes, value	$1,179,232	$4,560,084	$7,322,859
Wood pulp, tons	13,481	34,805	33,972
Photographic goods:			
Motion-picture films			
Not exposed, lin. ft.	155,359,550	57,995,064	90,398,122
Exposed, lin. ft.	32,690,104	84,557,376	188,527,165
Other sensitized goods, value	$1,348,216	$2,938,756	$4,960,928
Soap:			
Toilet or fancy, value	$2,141,633	$2,246,258	$6,625,259
All other, lbs.	58,547,763	82,726,757	155,891,586
Sugar and molasses:			
Molasses, gal.	1,002,441	3,811,341	7,667,830
Sirup, gal.	11,630,528	7,690,074	12,278,246
Sugar, refined, lbs.	50,895,726	576,415,850	1,444,030,665
Vulcanized fiber and manufactures of, value	$854,642	$950,029	$1,859,357
Washing powder and fluids, lbs.	12,761,958	4,754,084	6,217,201

[1] Not stated separately.

ORIGINAL PAPERS

THE DIRECT SYNTHETIC AMMONIA PROCESS*

By R. S. Tour

PLANT ONE SECTION, NITRATE DIVISION, ORDNANCE DEPT., U. S. A.

Received June 12, 1920

After much careful experimental work,[1] Prof. Fritz Haber, of Karlsruhe, Germany, patented[2] a process whereby nitrogen and hydrogen in the presence of a reaction promoter combined directly to form ammonia, according to the equation $N_2 + 3H_2 \rightleftarrows 2NH_3$. This is the basis of what has become known as the Haber process. The conditions necessary to bring about the combination to an appreciable extent, even in the presence of the best reaction promoters or catalysts so far developed, involve pressures of over 100 atmospheres, and temperatures over 500° C. The concentration of ammonia thus obtained in the nitrogen-hydrogen mixture, according to present practice, is of the order of 5 per cent. The catalytic synthesis is accomplished in one portion of a circulating system. The ammonia synthesized is removed continuously by liquefaction or absorption in another part of that system. The uncombined gases repeat the cycle after additional nitrogen and hydrogen have been introduced to replace that synthesized.

The nitrogen and hydrogen necessary for the synthesis may be obtained by any of several commercial methods. For the large quantities of hydrogen necessary in commercial installations of the Haber process, the water-gas oxidation method has proved the most suitable. This involves the production of water-gas and its further reaction with an admixture of steam in the presence of a catalyst according to the equation[3]

$$CO + H_2O \rightleftarrows CO_2 + H_2.$$

The nitrogen may be obtained in the mixture by injection of air during the manufacture or oxidation of the water-gas, or by the production of a pure producer gas to be mixed with the water-gas before oxidation.[4,5] The gas mixture after oxidation contains besides nitrogen and hydrogen large quantities of carbon dioxide, with some carbon monoxide. Extensive purification is necessary,[4,6,7] the carbon dioxide being removed by water washing at high pressures, the carbon monoxide by scrubbing with cuprous solutions, and incidental impurities by various special means. The purified gas, approximately three parts hydrogen and one part nitrogen, is then available for ammonia synthesis.

The complete process, including the manufacture of the gases, should be more properly known as the

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* Released by permission of the Chief of Ordnance.

[1] Numbers refer to References, p. 852.

FIG. 1—GENERAL VIEW OF GAS PLANT, U. S. NITRATE PLANT NO. 1

Haber-Bosch Process, crediting the development of the methods of manufacture of the pure gases to Dr. C. Bosch, of the Badische Anilin und Soda Fabrik of Ludwigshafen, Germany. A general outline of the process follows and indicates the order and the headings under which this paper will take up the various steps involved. A diagrammatic flow chart is shown in Fig. 2.

- I—PRODUCTION OF RAW GASES:
    - Water-Gas Manufacture
    - Producer-Gas Manufacture
    - Mixing of Producer- and Water-Gas
    - Direct Manufacture of Mixed Gas
- II—OXIDATION OF CARBON MONOXIDE:
    - Addition of Steam before Conversion
    - Heat Interchange and Catalysis
    - Cooling Gas and Condensation of Excess Steam
- III—PURIFICATION OF GAS:
    - Compression of Gas and Removal of Carbon Dioxide
    - Removal of Carbon Monoxide
    - Additional Purification
- IV—SYNTHESIS OF AMMONIA:
    - Adjustment of Gas Composition
    - Heat Interchange and Catalysis
    - Removal of Ammonia and Circulation of Gas

I—PRODUCTION OF RAW GASES

WATER-GAS MANUFACTURE—The water-gas process with standard equipment as used in the manufacture of illuminating gas is employed to decompose steam, producing free hydrogen along with oxides of carbon. In a subsequent paragraph it is shown how the carbon monoxide is utilized for the production of more hydrogen, and how the carbon dioxide is removed. The composition of the water-gas is given in Table I. It will be noted that 100 volumes of this mixture contain approximately 50 volumes of hydrogen as such and 40 volumes of potential hydrogen (later available) in the form of carbon monoxide, making a total of 90 volumes of hydrogen.

TABLE I—WATER-GAS COMPOSITION

	Operating Ranges		
	Per cent		Per cent
CO_2	5- 3		5- 3
CO	42- 45		42- 45
H_2	51- 50		53- 52
N_2	2	to	0
TOTAL,	100-100		100-100

PRODUCER-GAS MANUFACTURE—Standard methods of producer-gas manufacture may be employed to secure a gas mixture rich in nitrogen. Oxides of carbon are present, and, since some steam is used with the air, hydrogen also is present. Inasmuch as this producer-gas is later added to the water-gas, the hydrogen in the former, as well as the carbon monoxide (potential hydrogen), becomes available. The producer-gas may have the composition shown in Table II. The range of composition is wide, depending on the nature of the fuel and the operating conditions. One hundred volumes of this producer-gas represents approximately 60 volumes of nitrogen and 30 volumes of hydrogen as such or potential.

TABLE II—PRODUCER-GAS COMPOSITION

	Per cent
CO_2	5
CO	25
H_2	5
CH_4	2
N_2	63
TOTAL,	100

MIXING OF WATER- AND PRODUCER-GAS—To maintain the desired ratio of 3 parts of hydrogen (actual + potential) to one of nitrogen, a mixture of very nearly two volumes of water-gas to one volume of producer-gas of the above compositions would be required. The composition of the mixed gas is to a great extent independent of the compositions of the producer- and water-gases, if we assume that these gases have been mixed in proper proportion to secure the desired final ratio between the hydrogen and nitrogen. The final composition will, in normal practice, vary only within narrow limits, and should be as indicated in Table III. By solving the necessary fundamental equations the composition in the table may be deduced. One hundred volumes of this gas mixture contain about 70 volumes of actual and potential hydrogen and 23 volumes of nitrogen.

TABLE III—MIXED-GAS COMPOSITION

	Per cent
CO_2	3- 5
CO	39- 36
H_2	34- 36
N_2	23- 22
X (CH_4, argon, etc.)	1- 1
TOTAL,	100-100

DIRECT MANUFACTURE OF MIXED GAS—In lieu of making the two gases separately and mixing them in the desired proportions, the mixture may be made directly by the introduction of air into the water-gas machine during its "making" period.[4,6] The net result of this direct method is the combining of the water-gas machine and the producer in one apparatus.

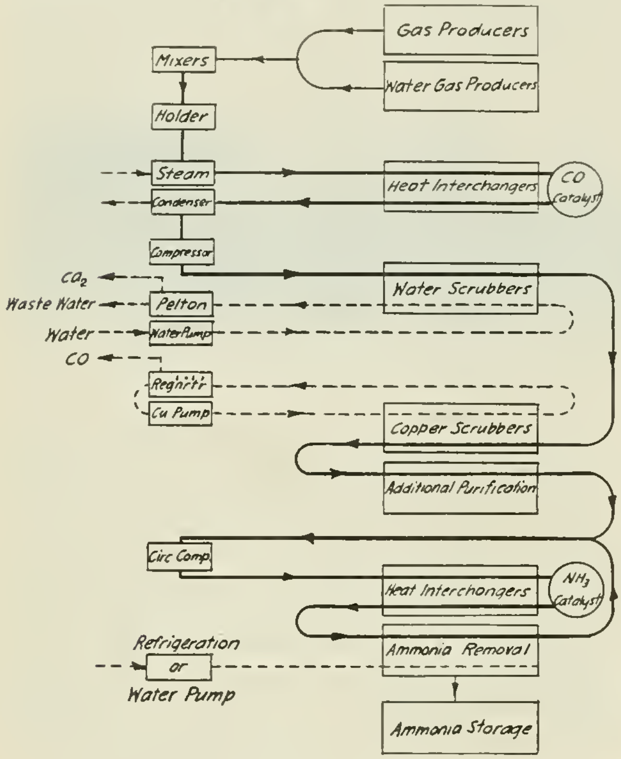

Fig. 2—Direct Synthetic Ammonia Process Flow Chart

A theoretical comparison leads to little choice, but operating considerations may definitely determine which of the methods to employ. Producers can use a lower grade fuel than water-gas machines, although in small plants duplication of apparatus may be the controlling factor.

II—OXIDATION OF CARBON MONOXIDE

ADDITION OF STEAM BEFORE CONVERSION—The carbon monoxide in the mixed gas will react with steam in the presence of a catalyst to produce carbon dioxide and hydrogen. This conversion is essentially a continuation of the reaction in the water-gas machine, under more favorable conditions of temperature and steam concentration.

Gas Generation $C + H_2O = CO + H_2$ (1)
CO Conversion $CO + H_2O = CO_2 + H_2$ (2)
Total Reaction (1) + (2) $C + 2H_2O = CO + 2H_2$ (3)

In the first reaction, in the absence of a catalyst, high temperatures prevail, and 100 per cent excess steam is good practice. In the converter with the aid of a catalyst a lower temperature is used with a many times greater excess of steam.

It can be shown theoretically that in the CO conversion reaction the unconverted carbon monoxide concentration in equilibrium varies inversely as the proportion of steam present and directly as a function of the temperature.[5] From Table IV it is evident that each additional volume of steam converts less additional carbon monoxide. In operation, therefore, a point of diminishing net return is quickly reached, depending mainly on the relative cost of the steam as compared to the later cost of carbon monoxide removal.

Table IV—Equilibrium Per cent CO
$(CO + H_2O \rightleftarrows CO_2 + H_2)$

Temp. ° C.	Inlet Steam per Volume of Inlet Gas 3 Vols. Per cent	 4 Vols. Per cent	 5 Vols. Per cent
400	0.45	0.33	0.26
450	0.80	0.58	0.46
500	1.25	0.91	0.71
550	1.80	1.31	1.03
600	2.45	1.78	1.40
650	3.20	2.32	1.83
700	4.05	2.94	2.24

HEAT INTERCHANGE AND CATALYSIS—The mixed gas containing nitrogen, hydrogen, and carbon monoxide is mixed with the necessary proportion of steam and forced through a set of heat interchangers, and on through the carbon monoxide converter wherein is a catalyst for the carbon monoxide conversion reaction. The catalysts are mainly of ferric oxide with an addition of some promoter.[9] Such catalysts are chemically rugged against poisons, although they are physically delicate. The gas, after passing the catalyst and carrying considerable excess steam (about 90 per cent of the initial steam), passes back through the heat interchangers, giving up its heat to the incoming mixture. The heat interchanging system is important since the temperature at the catalyst must be maintained between 400° and 600° C.,[5,9] the exact temperature depending upon the catalyst and operating conditions in general.

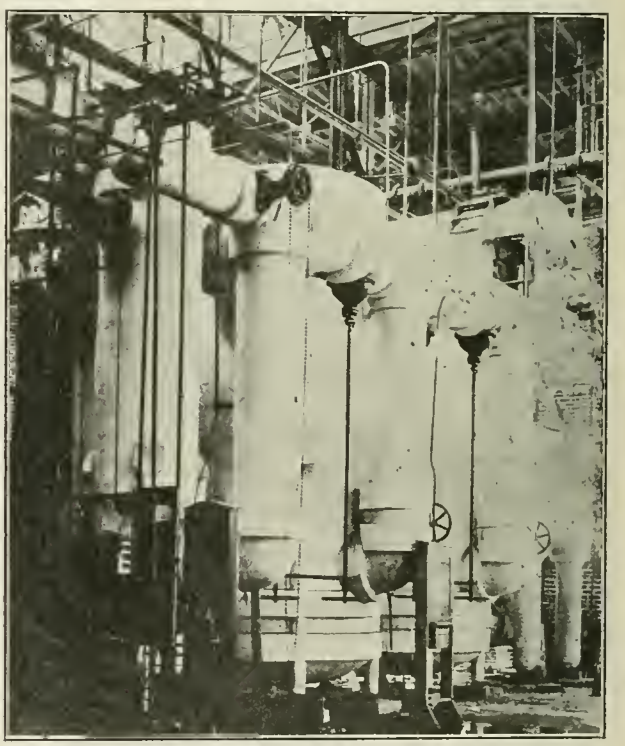

Fig. 3—Carbon Monoxide Converter and Heat Interchangers

The reaction of the carbon monoxide with steam is sufficiently exothermic to produce a rise of 50° to 60° C. during catalysis. With carefully designed heat interchangers of sufficient surface, the heat of reaction may offset radiation and heat losses, thus making the system self-maintaining in temperature. If the heat of reaction be insufficient, heat may be added by superheating the steam before admixture. However, any such external heat addition is inefficient, besides decreasing the temperature gradient across the heat interchangers. Heat may be developed more advantageously within the system by injecting air into the reacting gases, with consequent combustion either as a free flame or in the catalyst bed.[5]

If equilibrium were attained during catalysis, a gas would be secured containing but 1 to 2 per cent CO. In practice this is not reached, and 2 to 4 per cent CO remains, representing a conversion of about 90 per cent of the original carbon monoxide. Due to the conversion there is an increase of about one-third in the volume of the dry gases. The dry converted gas should have the composition shown in Table V. This analysis may also be obtained entirely by calculation.

TABLE V—GAS COMPOSITION (DRY) AFTER CONVERSION

	Per cent
CO_2	29– 27
CO	2– 4
H_2	52– 52
N_2	17– 17
TOTAL,	100–100
X (CH_4, argon, etc.)	0.4 to 0.8

COOLING GAS AND CONDENSATION OF EXCESS STEAM—The converted gas issues from the heat interchanger still at a somewhat elevated temperature. It is cooled and the excess steam condensed in special condensers. The composition of the gas mixture issuing from the condensers is then as given in the preceding paragraph.

III—PURIFICATION OF GAS

COMPRESSION OF GAS AND REMOVAL OF CARBON DIOXIDE—The chief impurity in the gas at this stage is carbon dioxide, which is removed by scrubbing the gas mixture with water at high pressures.[4,6,10] The dry gas is compressed in a multi-stage compressor up to the pressure at which it is to remain through the rest of the process, or perhaps to some intermediate pressure. The optimum pressure will depend on local operating conditions. For removal of the carbon dioxide the compressed gas is passed upward in a scrubber tower, countercurrent to water flowing downward over suitable packing. The composition of the washed gas at the exit of the scrubber is given in Table VI. If desired, the residual carbon dioxide (0.1 to 1.0 per cent) remaining after water scrubbing may be removed by washing the gas with a cold caustic solution.[11]

TABLE VI—GAS COMPOSITION AFTER WATER SCRUBBING

	Per cent
CO	3– 5
H_2	73– 72
N_2	24– 23
TOTAL,	100–100
CO_2	0.1 to 1.0
X (CH_4, argon, etc.)	0.5 to 1.0

The following points may be of interest: The solubility of carbon dioxide increases with its partial pressure. Table VII gives cubic feet of carbon dioxide at 60° F. and 30 inches Hg dissolved in 1 cu. ft. of water. For a given CO_2 percentage in a gas the scrubbing water necessary decreases with an increase of the total gas pressure. However, the energy required for pumping this decreased water at the increased pressure is not greatly altered. At a given total gas pressure, the quantity of solvent water necessary is not greatly affected by variations in CO_2 concentrations, since as the CO_2 to be dissolved decreases, the solubility also decreases. Hence, CO_2 absorption should be completed in one stage rather than in a series of stages at decreasing concentrations.

TABLE VII—SOLUBILITY OF CARBON DIOXIDE IN WATER[12]

CO_2 Partial Pressure Atmos.	0° C. Vols.	12° C. Vols.
5.0	9.2	6.5
10.0	17.1	10.3
15.0	23.6	14.5
20.0	28.6	18.2
25.0	32.5	21.6
30.0	36.0	24.8

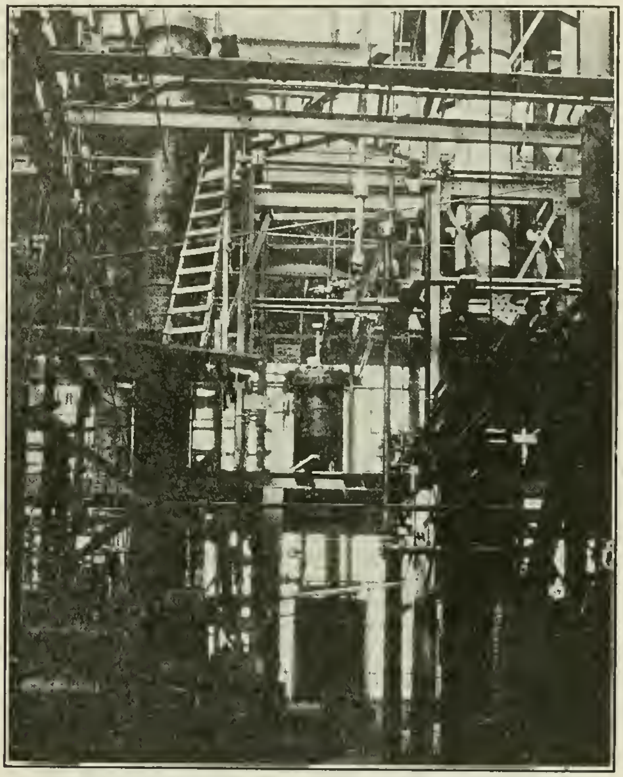

FIG. 4—DOUBLE WATER SCRUBBER TOWER SHOWING OTHER APPARATUS AND MAZE OF PIPING

The scrubbing water with its dissolved carbon dioxide (and hydrogen sulfide), as well as some hydrogen and nitrogen, passes from the bottom of the scrubbing tower and discharges through a water wheel.[4,6] Here the dissolved gases are liberated and much of the power used in pumping the water may be regenerated. The composition of the gas escaping from the dissolving water after pressure release will be normally as shown in Table VIII, the variation depending upon operating conditions.

TABLE VIII—COMPOSITION OF DISSOLVED GAS RELEASED FROM SCRUBBING WATER

	Per cent
CO_2	76– 84
H_2	17– 11
N_2	6– 4
X (H_2S, CO, etc.)	1
TOTAL,	100–100

The hydrogen and nitrogen dissolved represent about 10 per cent of the total of these gases being manufactured. This loss is theoretically independent of the pressure at which the scrubbing is done and is unavoidable since the solubility of hydrogen and nitrogen is not negligible. The carbon dioxide in the liberated gases is a valuable by-product. In conjunction with the ammonia synthesized, it may be used for the manufacture of ammonium sulfate by the decomposition of gypsum in the presence of ammonia, according to the equation

$$CaSO_4 + 2NH_3 + CO_2 + H_2O = CaCO_3 + (NH_4)SO_4,$$

or it can be used in the ammonia soda process:

$$2NaCl + 2NH_3 + CO_2 + 2H_2O = 2NaHCO_3 + 2NH_4Cl = Na_2CO_3 + CO_2 + H_2O + 2NH_4Cl.$$

There are available about 45,000 cu. ft. of carbon dioxide per ton of ammonia synthesized. This is much more than is necessary to satisfy the requirements per unit of ammonia in either of the above reactions. It is not within the scope of the present paper to discuss further the various special methods[13] of utilization of the main or by-products of the Haber process.

REMOVAL OF CARBON MONOXIDE—If an intermediate pressure has been used for water scrubbing the compression is completed and the gas passes through a scrubber similar to the water scrubber, but employing an ammoniacal cuprous solution[7] as the dissolving medium. The spent cuprous solution coming from the bottom of the scrubber passes on, after pressure release, to a regenerating system where its carbon monoxide is removed by heat. The composition of the solution may require readjustment before it is again used.

Scrubbing the gas with the ammoniacal cuprous solution removes by reaction with the reduced copper any oxygen that may be present; removes by combination with the free ammonia the carbon dioxide residual after the water scrubbing, as well as traces of other acidic gases that may have passed through the water scrubbers; and absorbs nearly all of the 3 to 5 per cent of carbon monoxide in the gas. Table IX gives the impurities in the gas leaving the copper system.

TABLE IX—IMPURITIES IN GAS AFTER CUPROUS SCRUBBING

	Per cent
CO_2	0
O_2	0
CO	0.1 –0.01
NH_3	0.2 –0.01
H_2O	0.02–less
X (CH_4, argon, etc.)	1.0 –0.5

Attempts have been made commercially to remove most of the carbon monoxide by a concentrated hot caustic solution[6,14] preliminary to the cuprous scrubbing. Carbon monoxide and hot caustic soda produce directly sodium formate. Chemically the carbon monoxide removal is satisfactory, reducing the 3 to 5 per cent inlet carbon monoxide down to under 1 per cent when the optimum caustic concentration of 10 per cent[15] is used at temperatures around 200° C. However, the residual carbon dioxide in the gas causes a precipitation of insoluble carbonate from the solution, and the mechanical difficulties are enormous. The consumption of caustic under operating conditions is prohibitive unless improved methods of recovery are developed.

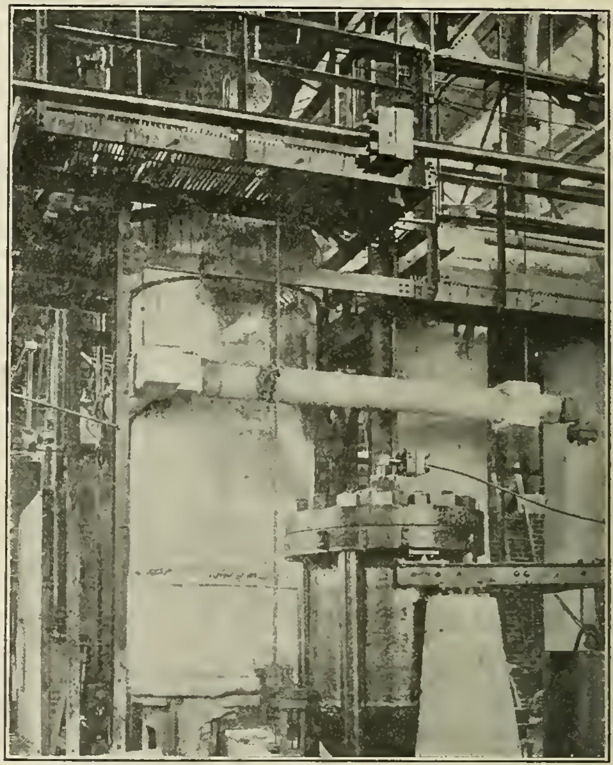

FIG. 5—AMMONIA CATALYST BOMB WITH HEAT INTERCHANGERS ON THE RIGHT

ADDITIONAL PURIFICATION—After the cuprous scrubbing, further purification may be necessary depending on the sensitiveness of the catalyst used for the ammonia synthesis. This purification may consist of refrigeration to remove most of the moisture, and in addition there may be some desiccating material, such as soda lime or sodamide,[6] following the cooler.

IV—SYNTHESIS OF AMMONIA

ADJUSTMENT OF COMPOSITION—The purified gas, consisting of about 3 parts hydrogen to 1 part nitrogen with 0.5 to 1.0 per cent of inert gases, such as argon and methane, passes into the ammonia circulating system. This is a separate and complete system wherein the entering gas acts as "make-up" to replace the gas synthesized and removed as ammonia. The uncombined gases after removal of ammonia repeat the cycle through the system together with the added "make-up." The supply of hydrogen and nitrogen to the circulating system should be in the average ratio of 3 : 1 to avoid the accumulation of the excess of either constituent. The chemical composition of the supply can evidently be best controlled by analysis of the gases in the circulating system where the cumulative effect of any slight inaccuracy of adjustment can be detected. The adjustment, if small, may be made by the injection of pure nitrogen or hydrogen obtained by liquefaction.[16] It is well to run toward high hydrogen in the supply so that the adjustment may be entirely with nitrogen.

Methane and argon to the amount of 0.5 to 1.0

per cent in the entering gases are inert at the operating temperatures and, therefore, tend to accumulate in the circulating system, and some method of removal must be employed. The simplest method is to allow a fraction of the circulating gases to escape. A purge of gas equal to 10 per cent of the "make-up" gas would maintain a concentration in the circulating system of 5 to 10 per cent inert gases. This purge involves a loss of pure gas, while high concentrations of inert gas involve decreased ammonia reaction. Hence, the amount of purge and consequent inert concentration must be determined by a consideration of operating costs.

HEAT INTERCHANGE AND CATALYSIS—The reaction for ammonia synthesis is:

$$N_2 + 3H_2 \rightleftarrows 2NH_3$$

The extent to which this reaction progresses depends upon the equilibrium of the system, which is a function of the temperature, pressure, and relative concentrations of the constituents. As in carbon monoxide conversion the equilibrium is more favorable at lower temperatures, although the reaction velocity is greatly decreased. The equilibrium is, however, favorably altered and also the reaction velocity increased by a rise in pressure. The effect of comparatively large variations from the ratio of 3 hydrogen to 1 nitrogen is small, although the maximum ammonia concentrations and greatest reaction velocities are obtained with the theoretical mixture. Table X shows the equilibrium ammonia concentrations for the reaction in a 3 : 1 mixture.[1]

TABLE X—EQUILIBRIUM NH_3 PER CENT

Temperature ° C.	30 Atm. Per cent NH_3	100 Atm. Per cent NH_3	200 Atm. Per cent NH_3
400	10.7	25.1	36.3
500	3.6	10.4	17.6
600	1.4	4.5	8.2
700	0.7	2.1	4.1

In the presence of a catalyst, reaction velocities are increased, so that a lower temperature with a more favorable equilibrium may be used. The equilibrium concentration of ammonia is not reached in practice. The activity of the catalyst will control the actual ammonia content, which seldom exceeds 5 per cent. The catalysts for this reaction as a class are very delicate chemically,[17] and small amounts of carbon dioxide, oxygen, or moisture greatly decrease their activity, while carbon monoxide is also quite harmful. The catalysts are mainly of reduced iron with various promoters added.[4,6,18]

With the present development of ammonia synthesis, temperatures of the order of 500° C. are employed. The reaction is exothermic to an extent sufficient to cause about a 15° C. temperature rise of the gases for each per cent of ammonia produced. The temperature gradient thus developed across the catalyst is available for maintaining heat interchange between exit and inlet gases through suitable apparatus. With proper design, sufficient heat interchange surface, and high conversion, the heat evolved in the reaction may offset all the heat losses. The supply of additional heat to the system is an important and serious problem.[19]

The construction of the apparatus in this portion of the system is an important problem. At high temperatures and pressures, hydrogen diffuses through steel in addition to decarburizing the metal and causing dangerous changes in its physical properties. Ammonia also has a deleterious effect, due probably to a nitrification of the iron. Various alloy steels, combined with special design of the apparatus, obviate much of the difficulty.[6,16,20]

REMOVAL OF AMMONIA AND CIRCULATION OF GAS—There are two distinct methods of ammonia removal:[6,21] one by liquefaction, the other by absorption. When employing liquefaction, the gas containing the ammonia passes from the converter heat interchangers through cold interchangers and into the liquefaction coils, externally and separately cooled by a refrigerating system. The ammonia gas is liquefied and may then be removed by mechanical separators or traps at the exit of the liquefiers, while the gas, still containing some residual ammonia, passes back through the cold interchangers and to the circulating pumps to repeat its cycle. The amount of residual ammonia in the gas will depend on the temperatures reached in the liquefier (Table XI).[22]

TABLE XI—VAPOR PRESSURE OF LIQUID NH_3

Temperature ° C.	NH_3 Vapor Pressure Atm.	NH_3 at 200 Atm. Per cent
0	4.2	2.1
—10	2.8	1.4
—20	1.83	0.91
—30	1.16	0.58
—40	0.68	0.34

FIG. 6—AMMONIA LIQUEFIER WITH AUXILIARIES

It is evident that very low temperatures are essential, especially with low ammonia conversion. Thus if 4 per cent ammonia is delivered by the catalyst at 100 atmospheres pressure with only —20° C. in the liquefier, nearly half the ammonia returns to the catalyst inlet. For the low temperatures necessary, special design and construction of the refrigerating system are required.

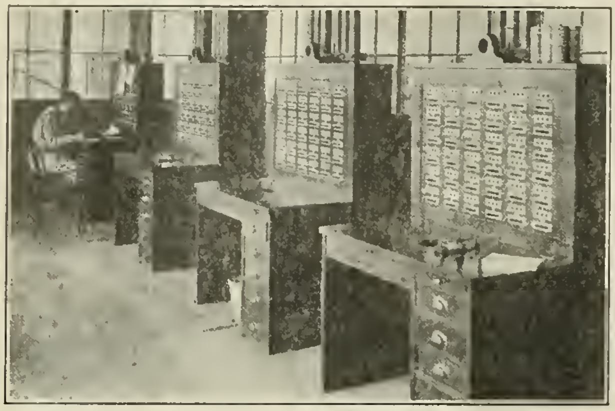

Fig. 7—Pyrometer Control Boards

If absorption of the ammonia be the method of removal, the gas mixture, still under pressure, is scrubbed with water. This is best done in several stages with efficient cooling throughout, since the heat of solution is very considerable. The absorption apparatus may consist of scrubber towers similar to the cuprous scrubbers, or it may consist of water-cooled coils through which the gas and absorbing water are forced in intimate mixture. The water may be discharged with an ammonia concentration corresponding to commercial aqua ammonia, or even higher if desired. The uncombined gases are recirculated to the heat interchangers and converter. The gas will contain an appreciable quantity of water vapor which will hinder catalytic activity and this point must be well considered. The residual ammonia in the gas will be very low, depending on the temperature of absorption. Table XII gives the ammonia and water vapor pressures of 25 per cent aqua.[23]

Table XII—Vapor Pressures of 25 Per cent Aqua Ammonia

Temperature ° C.	Vapor Pressure NH_3 Atm.	Vapor Pressure H_2O Atm.	Vol. at 200 Atm. NH_3 Per cent	Vol. at 200 Atm. H_2O Per cent
0	0.20	0.003	0.10	0.0015
+10	0.30	0.007	0.15	0.0035
+20	0.45	0.013	0.23	0.0065
+30	0.70	0.027	0.35	0.0135
+40	1.05	0.055	0.53	0.0275

Whichever method of ammonia removal is used, the quantity of gas to be circulated continuously per unit of ammonia extracted will be inversely proportional to the percentage of the gas removed as ammonia. The size of the system and design of piping, heat interchangers, ammonia removal installations, circulating pumps, etc., therefore, directly depend on the catalyst activity.

OPERATING QUANTITIES

Considering that gas, steam, water, and power are independently available, there follows an estimate of the quantities of these that will be necessary per short ton of ammonia for a Haber-Bosch process operating at 100 atmospheres and delivering 10 tons of liquid anhydrous ammonia per day.

(1) Raw Gas (M cu. ft.)	
Water-Gas	85
Producer-Gas	45
Total	130
(2) Low Pressure Steam (tons)	
CO Converters	14
Cuprous Regeneration	1
Total	15
(3) Water (M cu. ft.)	
CO Converter Condensers	9
CO_2 Scrubbers	7
Refrigerating Condensers	5
Additional	4
Total	25
(4) Power (k w. h.)	
Main Compressors	1200
Water Scrubber Pumps	800
Refrigerating Compressors	400
Gas Circulating Compressors	200
Additional	400
Total	3000

SYNTHETIC AMMONIA PLANT AT SHEFFIELD, ALABAMA

The American pioneers in the direct synthesis of ammonia on a manufacturing scale were the General Chemical Company. They had been experimenting extensively on catalysts for the ammonia reaction and had made tentative designs for the construction of a commercial unit before the United States entered the World War. Pursuant to Section 124, "Nitrate Supply," of an Act of Congress, a committee was appointed[24] to determine the best, cheapest, and most available means for the production of nitrates or other nitrogenous materials. The committee investigated the direct synthetic ammonia process as it was being developed at that time by the General Chemical Company, and after consultation with that company they recommended the following action:[25]

> 1—That the Government negotiate with the General Chemical Company for the right to use its synthetic ammonia process.
>
> 2—That contingent upon satisfactory result of such negotiations there be set aside from the $20,000,000 appropriation such a sum, estimated at about $3,000,000, as should be necessary to build a plant to produce by that process about 60,000 lbs. of ammonia per 24-hr. day.

In accordance with the above, arrangements were finally made whereby U. S. Nitrate Plant No. 1 was to be constructed according to the company's plans, but at government expense. The "National Defense Act" ruled that "the plant or plants provided for under this act shall be constructed and operated solely by the Government and not in conjunction with any other industry or enterprise carried on by private capital." Although construction and operation of the plant were by the Ordnance Department, U. S. A., the designs were furnished by the General Chemical Company, and construction as well as initial operation was carried out strictly under that company's supervision. Deviations in the process, modifications in apparatus, and changes in operating conditions were made only after consultation with, and approval of, the responsible engineers of the General Chemical Company stationed at the plant.

The total cost of Nitrate Plant No. 1 was about $13,000,000, which cost covered that of the nitric acid plant, the concentrating plant, ammonium nitrate plant, and the permanent village for officers and employees. The expenditure was only partly from the funds allotted under the National Defense Act. There is chargeable to synthetic ammonia manufacture only about $7,000,000 of the total. Perhaps an additional $1,000,000 should be charged for completing parts of the plant and installation. Based on the rated capacity of 60,000 lbs. of ammonia daily, the investment would amount to nearly $900 per annual ton of fixed nitrogen capacity.

The ammonia synthesis portions of the plant as installed consisted of three units, entirely independent of each other, not interconnected, but all under one roof. Unit No. 1, the only unit upon which operation was attempted, was rated at 15,000 lbs. of anhydrous ammonia per day. Unit No. 2 was a duplicate of No. 1, while Unit No. 3 was rated at 30,000 lbs. anhydrous ammonia per day. The total rated daily capacity of the plant was 30 tons of ammonia.

The process to be used was in general that discussed in the first part of this paper.[26] Operation was to be at 100 atmospheres pressure, or somewhat less, with ammonia removed by liquefaction. The raw gas mixture was to be made directly by the combined producer- and water-gas reactions. The carbon monoxide conversion was at atmospheric pressure with any necessary additional heat supply to be furnished by superheating the admixed steam, or by a free flame burning in the catalyst chamber. After condensation of the excess steam, compression to 100 atmospheres followed, which pressure was maintained through the rest of the system. The removal of carbon dioxide was to be accomplished in three stages, in series for the gas, with fresh water being supplied in parallel to each of the stages. The larger part of the carbon monoxide was to be removed by hot caustic solution, and the balance of that impurity by an ammoniacal cuprous carbonate solution. Final drying was accomplished by refrigeration followed by the use of desiccating material. In the circulating system additional heat was to be supplied to the gases entering the catalyst by a tubular heater similar to a steam superheater, and gas fired. The catalyst used was especially sensitive, being "composed of iron, sodium, and nitrogen."[1,18] The ammonia formed was to be removed by liquefaction, refrigeration being supplied by a standard ammonia expansion installation, and the liquefied synthetic ammonia being discharged to storage tanks provided for that purpose.

At the start of operations many difficulties immediately developed, and changes in process and apparatus became necessary. Initial operation of the plant commenced in June 1918 and the first synthetic ammonia was produced in September. Continuous operation was, however, never realized, and the plant was definitely closed in January 1919, after having produced only a small amount of ammonia. The raw gas manufactured finally developed into a practically straight blue water-gas, with most of the nitrogen added later as air for flame combustion in the carbon monoxide converter to maintain temperature there, while the overtaxed and inefficient steam superheaters were discarded. The compressors were quite satisfactory although under capacity when allowance was made for the hydrogen and nitrogen loss in the water scrubbers, in the inert gas purge, and in unavoidable leakage. The three water scrubbers operating with water in parallel gave much trouble and were inefficient in scrubbing and in water consumption, which difficulties were obviated by changing to a one-stage scrubbing. The removal of carbon monoxide with hot caustic involved many difficulties which were overcome only by the elimination of the caustic system with its towers, furnaces, pumps, etc. All the carbon monoxide was finally delivered to the cuprous solution for removal there. The cuprous system caused some difficulties and for improved absorption and efficiency reduced temperatures on both gas and solution were maintained. The purity of gas desired in view of the sensitiveness of the catalyst chosen was never obtained. In the circulating system the catalysis and heat interchange were not self-maintaining in temperature, and use of the high-pressure heating furnace installed for supplying additional heat was continually necessary, although it could not withstand the service for more than a few days at a time. Under-capacity of the refrigerating installation, excessive friction of gas circulation, and large unaccounted-for gas loss were some of the additional troubles in the circulating system. There were innumerable incidental mechanical difficulties with valves, with joints, with pressure gages, and with mechanical labor-saving devices. Experimenting and development stopped in January 1919, and negotiations looking toward an arrangement whereby the General Chemical Company should continue with this work for the Government were not successful.

As indicated above, many of the difficulties at U. S. Nitrate Plant No. 1 had been overcome by changes in the process or development of apparatus; many others can now be overcome in view of the past experience; and the balance can be overcome by additional experimenting and development. That final success can be hoped for is evident from the fact that in Germany there are two plants—one at Oppau with 100,000 tons of ammonia annual capacity, and one at Mercersburg with 200,000 tons rated capacity that were in regular operation during the war. The former was started just before the war, and extensive additions soon followed. The latter was built mainly during the war and three-fourths of the rated capacity was in operation before the armistice was signed.

The success of the German plants has shown that a process of this type may be successfully operated under war conditions. It has not yet been proved, although it seems probable, that it will be a commercial success under the post-war conditions that have arisen. All reports from Germany point to an optimistic feeling on the part of those connected with the industry there. No doubt the government has a very considerable interest in the German plants,[27] and probably a large amount of the capital cost and all of the experimental cost has been written off as a war expenditure.

Conditions in America are somewhat less favorable for the private operation of a Haber-Bosch plant than in Germany because of higher labor costs and greater installation charges. The determining factors may depend on the development of methods of utilization of the ammonia and by-products, which in turn may involve combinations with other known processes. In the German plants the combination of the ammonia-soda with the direct synthetic ammonia process has been accomplished with much success. This combination may be of far-reaching importance in the development of direct synthetic ammonia manufacture. In the United States, during the past year, the Solvay Process Company and the General Chemical Company have together formed the "Atmospheric Nitrogen Corporation," capitalized at $5,000,000, for the purpose of developing nitrogen fixation in this country. In Great Britain a corporation has been formed in which the Brunner-Mond Company (ammonia-soda process) is financially interested, and which has £5,000,000 available capital to design, build, and develop the direct synthetic ammonia process.

The situation with regard to private operation of a plant in this country does not apply to the government plant at Sheffield, Alabama, built as a war emergency measure. There the United States owns a complete plant designed to produce ammonia by a direct synthetic process. It had not reached an operative stage at the close of the war, and considerable alterations will have to be made before it can be considered operative. The Nitrate Division of the Ordnance Department, U. S. A., now has under way plans and redesigns for the modification of U. S. Nitrate Plant No. 1 to bring that plant to successful operation. This should by all means be done as a military preparedness measure. It will be recalled that Germany did not embark upon the World War until she had two independent nitrogen fixation processes—the cyanamide and the Haber—commercially developed. This country should not, after the lessons of the war, permit itself to be in a less favorable position than was Germany six years ago.

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GASOLINE FROM NATURAL GAS. III—HEATING VALUE, SPECIFIC GRAVITY, AND SPECIFIC HEAT

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The present paper of this series on natural-gas gasoline problems is devoted to a discussion of the following topics:

(1) Relationship between heating value and number of carbon atoms per molecule of hydrocarbon.

(2) Relationship between heating value and specific gravity of gasoline.

(3) Effect of removing gasoline upon heating value and specific gravity of natural gas.

(4) Specific heat of natural gas and gasoline vapor.

(1) RELATIONSHIP BETWEEN HEATING VALUE AND NUMBER OF CARBON ATOMS PER MOLECULE

If the assumption be made that the relationship between the heating value of normal paraffin hydrocarbons, expressed in calories per gram-molecule, and the number of carbon atoms per molecule is a linear one, it becomes a simple matter to compute tables of heating values that are valuable in the natural-gas gasoline industry. Such computations have been made for the heating values per lb., per gal., and per cu. ft. of vapor of the normal paraffin hydrocarbons, pentane to undecane, inclusive, and the results are incorporated in Table I. Thomsen's figures for the heating value of methane, ethane, and propane form the basis of the table and have been included in it.

Table I—Heating Values of Paraffin Hydrocarbons

A	B	C	D	E	F	G
Hydrocarbon	Calories per Gram-Mol.	B. t. u. per Lb.	Specific Gravity at 60° F.	Lbs. per Gal. at 60° F.	B. t. u. per Gal.	B. t. u. per Cu. Ft.
CH_4..........	211,900	23,790	..	...	...	1008.4
C_2H_6..........	370,400	22,200	..	...	...	1763.6
C_3H_8..........	429,200	21,620	..	...	...	2519
C_4H_{10}..........	...	21,320	..	...	...	3274
C_5H_{12}..........	...	21,130	0.6261	5.214	110,200	4029
C_6H_{14}..........	...	21,010	0.6627	5.519	116,000	4784
C_7H_{16}..........	...	20,920	0.6877	5.727	119,800	5540
C_8H_{18}..........	...	20,850	0.7067	5.885	112,700	6295
C_9H_{20}..........	...	20,800	0.7222	6.014	125,100	7050
$C_{10}H_{22}$..........	...	20,760	0.7342	6.114	126,900	7805
$C_{11}H_{24}$..........	...	20,730	0.7427	6.185	128,200	8560

Column B—Thomsen's figures for the hydrocarbons, methane, ethane, and propane (Landolt-Börnstein, "Physikalisch-chemische Tabellen," **1912**, p. 909).

Column C—The figures in Column C were obtained from the formula

$$\text{B. t. u. per lb.} = \frac{20{,}375n + 6832}{n + 0.1438} \text{ (see Equation 4 of text)}$$

Column D—The specific gravities in Column D are the same as those given in Part I of this series (This Journal, **12** (1920), 548), except that they are here carried out to four places.

Column E—Lbs. per gal. at 60° F. in Column E were obtained by multiplying the specific gravities in Column D by 8.328, the weight of 1 gal. of water at 60° F.

Column F—The values in Column F were obtained by multiplying the values in Column E by those in Column C.

Column G—B. t. u. per cu. ft. at 60° F., 30 inches mercury, dry gas, as given in Column G, were computed from the formula H.V. = $755.2n + 253.2$ (see Equation 6 of text).

According to the assumption that has been made, the relationship between calories per gram-molecule and carbon atoms per molecule for the normal paraffin hydrocarbons may be expressed by an equation of the form

$$\text{Cal. per gram-molecule} = an \pm b \qquad (1)$$

where n represents the number of carbon atoms per molecule. Thomsen's values given in Table I were substituted in this equation with the proper values for n, and by the method of least squares a and b were evaluated, giving the equation[1]

$$\text{Cal. per gram-molecule} = 158{,}650n + 53{,}200 \qquad (2)$$

Substitution of values of n from 1 to 3 in this equation gives heating values within 0.03 per cent of the values given by Thomsen.

Since heating value expressed in B. t. u. per lb. may be obtained from calories per gram-molecule by dividing by the molecular weight of the hydrocarbon and multiplying by the factor 1.8, the relationship between B. t. u. per lb. and carbon atoms per molecule may be expressed by the formula

$$\text{B. t. u. per lb.} = 1.8\left(\frac{158{,}650n + 53.200}{14.016n + 2{,}016}\right) \qquad (3)$$

where $14.016n + 2.016$ represents the molecular weight of the hydrocarbon in terms of the number of carbon atoms. Equation 4 is a simplified form of Equation 3.

$$\text{B. t. u. per lb.} = \frac{20{,}375n + 6832}{n + 0.1438} \qquad (4)$$

The heating value of these hydrocarbons may be expressed on the basis of volume by the formula

$$\text{B. t. u. per cu. ft. at 60° F., 30 inches mercury, dry} = \frac{(20{,}375n + 6832)\ (0.037065n + 0.00533)}{n + 0.1438} \qquad (5)$$

where the expression $0.037065n + 0.00533$ represents the weight of 1 cu ft. of gas at 60°, 30 inches mercury, dry, in lbs. Since this expression is equivalent to $0.037065\ (n + 0.1438)$, Equation 5 may be reduced to the following form:

$$\text{B. t. u. per cu. ft. at 60°, 30 inches mercury, dry} = 755.2n + 253.2 \qquad (6)$$

This equation differs somewhat from the one employed in a previous article,[1] which is

$$\text{B. t. u. per cu. ft. at 60° F., 30 inches mercury, dry} = 754.7n + 253.8. \qquad (7)$$

Equation 7 was derived from a consideration of Thomsen's figures for methane and ethane only and is probably less nearly correct than Equation 6 for values of n greater than 2. The difference between the values obtained by substituting various values of n in the two formulas increases, of course, with increase in the value of n, but amounts to less than 0.1 per cent for undecane.

It is evident that the heating values given in Table I are for hydrocarbons in vapor form and the latent heat of vaporization must be subtracted from these values if heating values of the liquids are desired. Some idea of the accuracy of these computed values may be obtained by comparing the computed heating value of normal octane with that determined by Richards and Jesse.[2] The computed heating value of normal octane is 20,850 B. t. u. per lb., while that obtained by Richards and Jesse amounts to 20,560 B. t. u. per lb. Subtracting 130 B. t. u. for the latent heat of vaporization[3] from the computed value reduces it to 20,720 B. t. u. per lb., which is about 0.8 per cent higher than the observed value.

(2) RELATIONSHIP BETWEEN HEATING VALUE AND SPECIFIC GRAVITY OF GASOLINE

If the heating value of the various gasoline hydrocarbons, expressed in B. t. u. per lb., be plotted against specific gravity as shown in Fig. 1, it will be found that the points lie very nearly on a straight line.[4] By the method of least squares it was found that the equation

$$\text{B. t. u. per lb.} = 23{,}330 - 3500\ G \qquad (8)$$

represents the relationship between heating value and specific gravity very closely. If the values for specific gravity given in Column D of Table I be substituted for G in this equation, the heating values obtained agree within 0.03 per cent of those given in Table I.

B. t. u. per gal. at 60° F. may be obtained from B. t. u. per lb. by multiplying by 8.328 G, as shown in Equation 9.

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[1] Since this was written, it has been learned that LeBas (*Proc. Chem. Soc. Lond.*, **23**, 134; *Chem. News*, **110**, 26, 37) has suggested the equation

$$\text{Cal. per gram-molecule} = K\ (6n + 2)$$

to correlate the heating values of the various gaseous paraffin hydrocarbons. The ratio of 53,200 to 158,650 is that of 1 to 2.982, and the value of K which gives the correct value for methane gives a result only 0.17 per cent higher for undecane than that obtained from Equation 2.

[1] This Journal, **12** (1920), 548.

[2] *J. Am. Chem. Soc.*, **32** (1910), 268; corrected in **36** (1914), 248.

[3] Longuinine, *Compt. rend.*, **121** (1895), 557.

[4] Since the linear relationship holds closely for specific gravity and B. t. u. per lb., the formula which correlates specific gravity and carbon atoms per molecule must be similar to the one which correlates B. t. u. per lb. and carbon atoms per molecule. The method of least squares gave the formula

$$G = \frac{11.82n - 13.89}{14.016n + 2.016} = \frac{0.8433n - 0.9907}{n + 0.1438}.$$

where G represents the specific gravity of the hydrocarbon in liquid form. Substitution of different values of n between 5 and 11 gives values for the specific gravity of the various hydrocarbons that agree with the values given in Table I to within 0.0005, except in the case of pentane where the difference is 0.001, and in the case of undecane where the difference is 0.0008.

$$\text{B. t. u. per gal. at } 60^\circ \text{ F.} = (23{,}330 - 3500\,G)\,8.328\,G \quad (9)$$

The curve represented by Equation 9 does not differ much from a straight line over the range involved (see Fig. 1), and the linear equation

$$\text{B. t. u. per gal. at } 60^\circ \text{ F.} = 14{,}200 + 153{,}500\,G \quad (10)$$

gives heating values of the various hydrocarbons within 0.04 per cent of those in Table I, except in the case of pentane where the difference is 0.1 per cent.

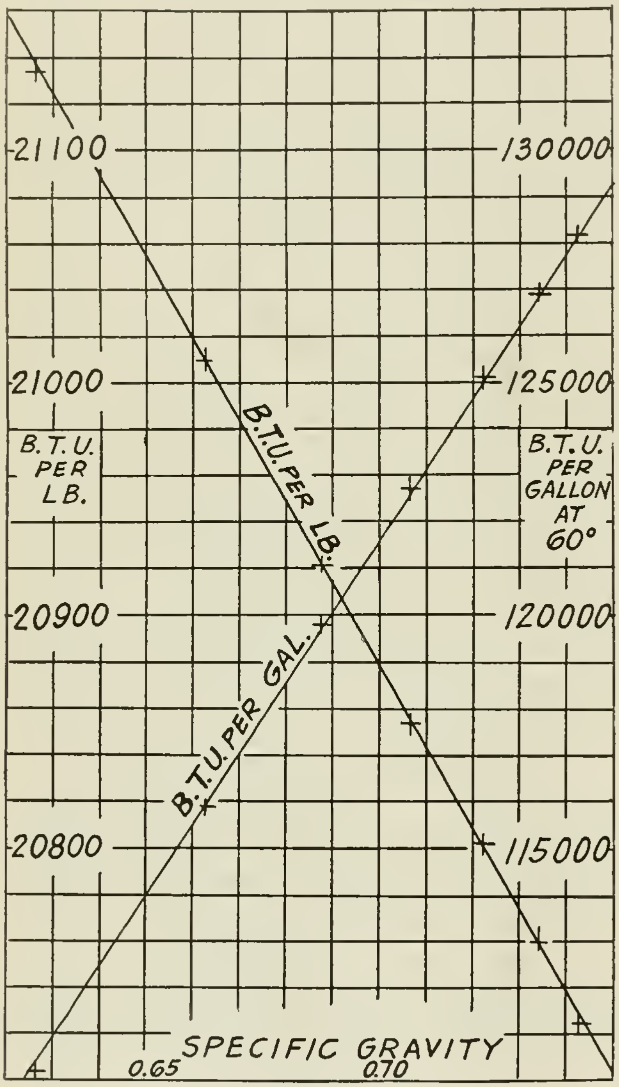

Fig. 1

Equations 8 and 10 are directly applicable to gasoline, providing the assumption be made that it consists only of the normal paraffin hydrocarbons, pentane to undecane, inclusive. In other words, the formulas do not hold merely for the various individual hydrocarbons, but also for various mixtures of these hydrocarbons which might exist as gasoline. The composition of gasoline of a certain specific gravity might vary considerably as to the number and relative proportions of the various constituents, but, under the assumption that has been made, this would have no material effect upon the heating value of the gasoline expressed either in B. t. u. per lb., or in B. t. u. per gal.

On the other hand, the specific gravity of a gasoline does not define exactly the average number of carbon atoms per molecule, the specific gravity of its vapor, the heating value of its vapor in B. t. u. per cu. ft., or the volume of vapor required to produce one gallon of gasoline, since the relationships between these characteristics and specific gravity are curvilinear.

While the statements in this section apply strictly only to mixtures of the normal paraffin hydrocarbons, they probably apply quite closely to natural-gas gasoline and straight-run gasoline, since substances belonging to other than the paraffin series would be present only in very small amounts, and the presence of the isomeric forms of the various paraffin hydrocarbons would have but very little disturbing effect.

(3) EFFECT OF REMOVING GASOLINE UPON VOLUME, HEATING VALUE, AND SPECIFIC GRAVITY OF NATURAL GAS

The question as to the effect of removing gasoline upon the heating value and specific gravity of natural gas is one of especial interest to natural-gas companies and to natural-gas consumers. At the present time, many users of natural gas feel that their gas has been greatly deteriorated by the extraction of gasoline from it. This opinion is not usually justified but is the natural result of ignorance as to just what change has taken place. The consumer is familiar perhaps with some compression plant which is operating on gas whose gasoline content is high, and where the effect upon the gas volume and heating value is appreciable, and does not realize that the gas produced by the gas company is usually of a different sort and contains but little gasoline.

The reduction in volume due to the removal of gasoline vapor from natural gas depends primarily upon the yield and specific gravity of the gasoline that is produced; the reduction in heating value primarily upon the heating value of the gas, and upon the yield and specific gravity of the gasoline removed; and the reduction in specific gravity primarily upon the specific gravity of the gas, and upon the yield and specific gravity of the gasoline removed. It is not a difficult matter to determine experimentally what the change in volume, heating value, and specific gravity amounts to in any given case, unless the change is extremely small, but it is frequently not convenient to do so. It is also unnecessary, since this change can be computed with sufficient accuracy for all ordinary purposes if the necessary information is available.

In making the computation, the relationship between the specific gravity of the gasoline and (*a*) the specific gravity of its vapor, (*b*) the quantity of vapor required to produce a gallon of gasoline, and (*c*) the heating value of this vapor in B. t. u. per cu. ft. must first be established. This can be done conveniently with the aid of a diagram such as is shown in Fig. 2, where specific gravity of vapor is plotted against specific gravity of liquid for pentane, hexane, and heptane.[1] Let it be assumed that the gasoline produced from the natural gas has a gravity of 90° Bé.

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[1] Data from first article of this series, Table I, This Journal, 12 (1920), 548.

(= 0.6364 sp. gr.). Where the pentane-hexane line crosses the line of 90° Bé. gasoline, the specific gravity of the vapor is 2.627, and the gasoline composition 71.9 per cent C_5H_{12} and 28.1 per cent C_6H_{14}. Where the pentane-heptane line crosses the line of 90° Bé. gasoline, the specific gravity of the vapor is 2.653, and the gasoline composition 83.3 per cent C_5H_{12} and 16.7 per cent C_7H_{16}. The average specific gravity of vapor is 2.64, which corresponds to a composition of 77.6 per cent C_5H_{12}, 14.1 per cent C_6H_{14}, and 8.3 per cent C_7H_{16}. This appears to be a reasonable composition for 90° Bé. gasoline from natural gas except that it does not provide for the small percentages of butane, octane, nonane, etc. The maximum possible variation in the value for specific gravity of vapor from the value 2.64 is ±0.49 per cent if only pentane, hexane, and heptane be considered. Table II contains information obtained in this fashion for 75, 80, 85, and 90° Bé. gasoline, both as to specific gravity of vapor and as to cu. ft. vapor per gal.

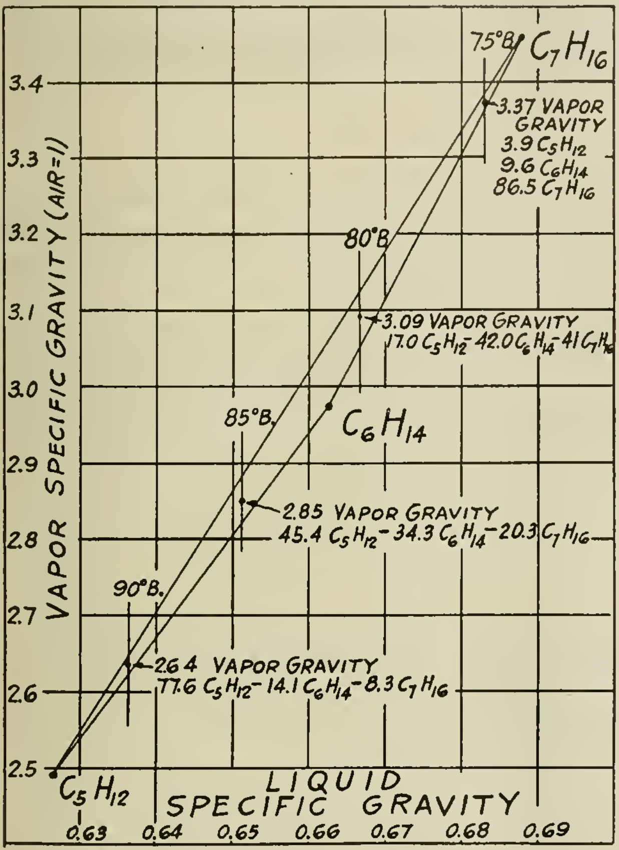

FIG. 2

TABLE II

GRAVITY ° Bé.	Average of Max. and Min. Sp. Gr. of Vapor	Max. Error of Sp. Gr.	Percentage Composition Corresponding to Sp. Gr. C_5H_{12}	C_6H_{14}	C_7H_{16}	Cu. Ft. Vapor per Gal. of Mixture	Max. Error of Vol. Vapor	
90	2.64	±0.5	77.6	14.1	8.3	26.4	±0.2	
85	2.85	±1.1	45.4	34.3	20.3	25.1	±0.4	C_5H_{12}, C_6H_{14}
80	3.09	±1.2	17.0	42.0	41.0	23.7	±0.5	C_7H_{16} mixtures
75	3.37	±0.2	3.9	9.6	86.5	22.1	±0.1	

Similar data have been obtained for mixtures of butane,[1] pentane, and hexane in the case of 85° and 90° Bé. gasoline, and for mixtures of hexane, heptane, and octane in the case of 75° and 80° Bé. gasoline. This information is contained in Table III.

TABLE III

GRAVITY ° Bé.	Average of Max. and Min. Sp. Gr. of Vapor	Max. Error of Sp. Gr.	Percentage Composition Corresponding to Sp. Gr.			Cu. Ft. Vapor per Gal. of Mixture	Max. Error of Vol. Vapor	
			C_4H_{10}	C_5H_{12}	C_6H_{14}			
90	2.66	±2.1	15.0	35.9	49.1	26.4	±0.2	C_4H_{10}, C_5H_{12}
85	2.83	±0.4	6.6	15.7	77.7	25.1	±0.1	C_6H_{14} mixtures
			C_6H_{14}	C_7H_{16}	C_8H_{18}			
80	3.06	±0.2	87.5	8.0	4.5	23.8	0.0	C_6H_{14}, C_7H_{16}
75	3.39	±0.8	36.6	40.4	23.0	22.1	±0.1	C_8H_{18} mixtures

The figures given in Table IV for specific gravity of vapor and cu. ft. of vapor per gal. represent the average of the values given in Tables II and III. The heating values in the table have been computed from the specific gravities of the vapor by means of the formula

B. t. u. per cu. ft. at 60°, 30 inches mercury, dry =

$$1559.7\ G_v + 144.6,$$

this procedure being permissible on account of the linear nature of the heating value—specific gravity relationship (G_v = specific gravity of vapor).

TABLE IV

GRAVITY ° BÉ.	Probable Specific Gravity of Vapor	Probable Heating Value B. t. u. per Cu. Ft.	Probable Volume Vapor per Gal. Cu. Ft.
90	2.65	4278	26.4
85	2.84	4574	25.1
80	3.07	4933	23.7
75	3.38	5416	22.1

It seems reasonable to assume that the values in Table IV apply quite closely (probably within 1 per cent) to the ordinary natural-gas gasoline. With these values established the computation of the change in heating value or specific gravity of any natural gas may easily be carried out.

The relationship between heating value of gas before and after gasoline extraction is given by the formula

$$\text{H. V. untreated gas} \times 100 = \text{H. V. treated gas} \times (100 - V) + \text{H. V. gasoline vapor} \times V \qquad (11)$$

or H. V. treated gas =

$$\frac{\text{H. V. untreated gas} \times 100 - \text{H. V. gasoline vapor} \times V}{100 - V} \qquad (12)$$

where V represents the volume of gasoline vapor removed.

Similarly, sp. gr. treated gas =

$$\frac{\text{Sp. gr. untreated gas} \times 100 - \text{sp. gr. gasoline vapor} \times V}{100 - V} \qquad (13)$$

Figs. 3 and 4 show the percentage loss in heating value and specific gravity, respectively, as a result of the removal of different amounts of 90° Bé. gasoline from different grades of natural gas.[1] The effect of

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[1] Theoretical sp. gr. of butane at 60° F. = 0.575, and cu. ft. vapor per gal. = 31.2.

[1] In preparing these curves, the possible effect of butane in 90° Bé gasoline upon the specific gravity and heating value of the vapor was ignored. This accounts for the difference between the values employed and those given in Table IV. The effect of changing the specific gravity of the vapor from 2.64 to 2.65 and the heating value of the vapor from 4263 to 4279 is slight, modifying the per cent decrease in specific gravity from 11.53 per cent to 11.67 per cent for a gasoline removal of 5 gal. per M cu. ft. from gas of 1.50 specific gravity. Present indications are that 90° Bé. gasoline from natural gas contains appreciable amounts of butane even after distillation, and the probable presence of this constituent was taken into account in preparing Table IV.

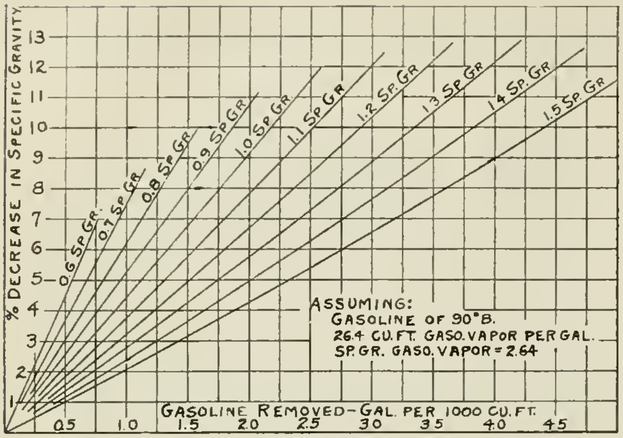

Fig. 3

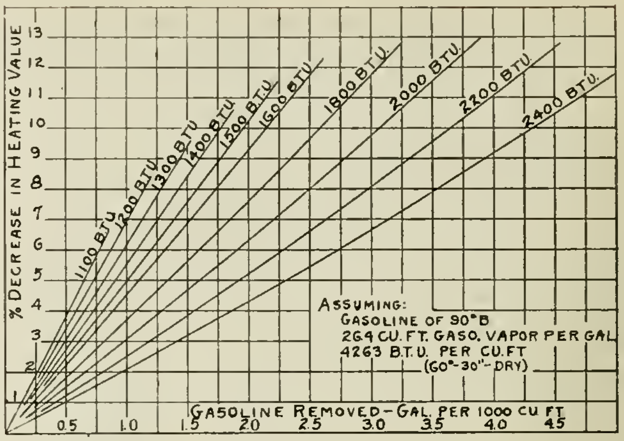

Fig. 4

increasing the Baumé gravity of the gasoline produced from natural gas is to decrease the change in heating value and specific gravity of the gas, the amount produced being kept constant. This effect is small, however.

A very large percentage of the natural gas produced in this country contains less than 0.5 gal. gasoline per 1000 cu. ft., and reference to the figures will show that the change in heating value and specific gravity is usually quite small.

The obvious purpose of Fig. 3 is to make possible the determination, in a simple and fairly accurate manner, of the loss in heating value of natural gas as a result of extraction of gasoline by any of the methods in common use. It can be used in figuring the loss to the consumer in the heating value of gas that has been treated only when conditions are such that the untreated gas could be transported from the point of production to the point of consumption without gasoline condensation. Very frequently this unavoidable condensation of gasoline is large and of considerable importance in attempting to determine to what extent the extraction of gasoline as a commercial project affects the gas as it finally reaches the consumer.

(4) SPECIFIC HEAT OF NATURAL GAS AND GASOLINE VAPOR

The specific heat of methane at constant pressure is generally taken as equal to 0.5929. So far as is known, the specific heat in vapor form of the other hydrocarbon constituents of natural gas has not been determined. On account of this lack of information, a relationship between the specific heat of a mixture of paraffin hydrocarbon gases and the number of carbon atoms per molecule has been worked out, based upon the assumption that the molecular heat of a paraffin gas divided by the number of atoms in the molecule equals a constant.

For methane the constant is

$$\frac{0.5929 \times 16.032}{5} = 1.90,$$

and for a mixture of paraffin gases, according to the assumption that has been made, the relationship is

$$H_p \times \frac{12n + 2.016n + 2.016}{3n + 2} = 1.90 \qquad (14)$$

or

$$H_p = \frac{1.90\,(3n + 2)}{14.016n + 2.016} = \frac{0.4067n + 0.2711}{n + 0.1438} \qquad (15)$$

where H_p represents specific heat at constant pressure, and n represents the number of carbon atoms per molecule of hydrocarbon.

If it is desired to correlate specific heat and specific gravity of natural gas, Equation 16[1] may be combined with Equation 15 to eliminate n, thus obtaining Equation 17. Equations 16 and 17 are subject to the assumption that the natural gas contains only paraffin gases.

$$n = \frac{G_{gas} - 0.0696}{0.4842} \qquad (16)$$

$$H_p = 0.407 + \frac{0.103}{G_{gas}} \qquad (17)$$

Equation 17 may be modified so as to give the volumetric specific heat of natural gas by multiplying it by 0.0765 G_{gas}, the weight in lbs. of one cu. ft. of the gas at 60° F., 30 inches mercury, dry. In this way Equation 18 is obtained.

$$H_p \text{ per cu. ft.} = 0.031\ G_{gas} + 0.008 \qquad (18)$$

Table V contains the specific heats by weight and by volume, at constant pressure, of the important constituents of natural gas as computed from Equations 17 and 18.

Table V

Hydrocarbon Gas	Specific Gravity (Air = 1)	Sp. Heat at Constant Pressure	Vol. Sp. Heat at Constant Pressure (Eng. Units)
Methane	0.554	0.593	0.025
Ethane	1.038	0.506	0.040
Propane	1.523	0.475	0.055
Butane	2.007	0.458	0.070
Pentane	2.491	0.448	0.085
Hexane	2.975	0.442	0.100
Heptane	3.459	0.437	0.115
Octane	3.944	0.433	0.130
Nonane	4.428	0.430	0.145
Decane	4.912	0.428	0.160
Undecane	5.396	0.426	0.175

In employing Equations 17 and 18, or the values given in Table V, the limiting assumptions must be kept constantly in mind. As stated before, the assumptions are: (1) that the molecular heat of a paraffin gas divided by the number of atoms in the molecule equals a constant, and (2) that the natural gas contains only paraffin gases.

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[1] Anderson, This Journal, 11 (1919), 299.

With regard to the first assumption, it appears quite probable that the relationship mentioned holds quite accurately for ethane. If this be true, the equations that have been worked out would apply to natural gases where the average number of carbon atoms per molecule is less than 2, and most natural gases would be included in this class. The applicability of the formulas to rich natural gases and gasoline vapor is problematical, and experimental proof of the accuracy of the basic assumption is needed. It will be noted that the specific heat of the hydrocarbons that constitute gasoline ranges from 0.426 to 0.448. This is considerably less than the value of 0.5 that is generally employed for gasoline in liquid form.

The assumption as to the composition of the natural gas has been made purely for convenience. If analysis shows constituents other than paraffin gases, it is a simple matter to make the necessary corrections.

SUMMARY

I—Formulas have been developed to correlate the following characteristics of normal paraffin hydrocarbons:

Calories per gram-molecule and number of carbon atoms per molecule	(2)
B. t. u. per lb. and number of carbon atoms per molecule	(4)
B. t. u. per cu. ft. and number of carbon atoms per molecule	(6)
B. t. u. per lb. and specific gravity in liquid form	(8)
B. t. u. per gal. and specific gravity in liquid form	(10)
Specific gravity in liquid form and number of carbon atoms per molecule	(Note)
Specific heat and number of carbon atoms per molecule	(15)
Specific heat and specific gravity in gaseous form	(17)
Volumetric specific heat and specific gravity in gaseous form	(18)

II—The relationships between specific gravity and B. t. u. per lb. and per gal. may be expressed quite accurately by linear equations. The significance of this is that the specific gravity of a mixture of normal paraffin hydrocarbons determines its heating value, expressed either in B. t. u. per lb. or B. t. u. per gal., regardless of what variation may take place in the number and proportions of constituents. This statement applies to gasoline in so far as gasoline is a mixture of the normal paraffin hydrocarbons.

III—Probable values of the heating value and specific gravity of vapor, and volume of vapor per gallon have been computed for four different grades of gasoline.

IV—Figures have been prepared showing the change in the heating value and specific gravity as a result of the extraction of different amounts of 90° Bé. gasoline from different grades of natural gas.

ALKALI FUSIONS. II—THE FUSION OF SODIUM BENZENE *m*-DISULFONATE WITH SODIUM HYDROXIDE FOR THE PRODUCTION OF RESORCINOL[1]

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In a paper[2] recently published from this laboratory, there were given results of a series of experiments ascertaining the proper conditions for obtaining the highest yield of carvacrol by the fusion of sodium *p*-cymene sulfonate with sodium hydroxide. In connection with these experiments an apparatus was devised especially suited to the study of alkali fusion of aromatic sulfonic acids. Using this apparatus we have now completed a similar study of the production of resorcinol by the fusion of sodium benzene *m*-disulfonate with sodium hydroxide.

Although this subject has received attention from a number of investigators, a survey of the literature shows quite conclusively that, with possibly one exception, no systematic study of this problem has been made. There appears to be no agreement among those who have contributed to this subject as to the proper method of conducting an alkali fusion of sodium benzene *m*-disulfonate in order to get the best yield of resorcinol. The recorded yields vary from about 20 to 100 per cent.

HISTORICAL REVIEW

Among the earliest contributions on this subject those of Garrick[1] and V. Meyer[2] may be mentioned. The former claimed to have obtained an almost quantitative yield of resorcinol by the fusion of sodium benzene *m*-disulfonate with potassium hydroxide for 2 to 3 hrs. at 230°. V. Meyer in his paper gives no details as to method or yield.

Barth and Senhofer[3] obtained a 90 to 95 per cent yield of resorcinol by fusing sodium benzene *m*-disulfonate with potassium hydroxide, but failed to describe just how the fusion was conducted. The same authors in a second paper[4] stated that an almost theoretical yield of resorcinol was obtained by fusing the potassium salt of benzene *m*-disulfonic acid with potassium hydroxide, but again failed to give any details as to their method.

Durand[5] gave the following directions for making resorcinol: The sodium salt of benzene *m*-disulfonic acid is fused for from 24 to 36 hrs. with five times its weight of sodium hydroxide (35 moles) in an iron pot provided with a mechanical stirring device and heated in an oil bath. The melt is dissolved in water, acidulated with sulfuric acid, and extracted with ether. No data are given as to the yield or the temperature at which the fusion is conducted.

Binschedler and Busch[6] gave a description of the process of making resorcinol then commercially in use. Sixty kilos of sodium benzene *m*-disulfonate were added to 150 kilos (17.6 moles) of molten sodium hydroxide, containing as little water as possible, and fused for from 8 to 9 hrs. at 270°. An almost theoretical yield of resorcinol was claimed.

Degener[7] was the first to make a study of the various conditions affecting the yield of resorcinol, such as temperature and time of fusion, proportion of alkali to be used, and the effect of substituting sodium hydroxide for the potassium compound. He came to the conclusion that potassium hydroxide was somewhat better than sodium hydroxide and that a mixture of one mole of each of these two alkalies was nearly as satisfactory as pure potassium hydroxide. The optimum temperature when potassium hydroxide was used for the fusion was from 250° to 255°, whereas with sodium hydroxide the best yields were obtained at from 270° to 280°. The results also indicated that 12 moles of alkali to one of sodium benzene *m*-disulfonate were sufficient, and that 20 min. was the most favorable fusion period. In general, the yields were low, the best being 25.94 per cent of the theory. The fact that all the fusions were conducted below 280° undoubtedly accounts, to some extent, for the low yields.

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[1] Presented at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

[2] This Journal, **12** (1920), 145.

[1] *Z. Chem.*, **1869**, 549.

[2] *Ber.*, **7** (1874), 1308.

[3] *Ann.*, **174** (1874), 235.

[4] *Ber.*, **8** (1875), 1477.

[5] *Mon. Sci.*, **18** (1876), 696.

[6] *Ibid.*, **20** (1878), 1169.

[7] *J. prakt. Chem.*, [2] **20** (1879), 300.

Mülhauser[1] described the commercial process for making resorcinol. Two hundred and fifty kilos of sodium hydroxide (14.1 moles), 10 kilos of water (4 per cent of the weight of the sodium hydroxide), and 125 kilos of sodium benzene *m*-disulfonate are fused in an open pot provided with a stirrer. The reaction is said to be complete when the mixture becomes quiet. A yield of 20 to 23 kilos of resorcinol (41 to 47.2 per cent of the theory) is obtained.

The commercial process for making resorcinol as described by Schoop[2] is essentially the same as the foregoing, the only difference being that he prescribes 230 kilos of sodium hydroxide to 125 kilos of sodium benzene *m*-disulfonate. He claims, however, that from 125 kilos of sodium benzene *m*-disulfonate, 48 to 50 kilos of resorcinol were obtained. Inasmuch as the theoretical yield is 48.7 kilos, his figures are obviously too high.

MATERIALS AND APPARATUS

SODIUM BENZENE *m*-DISULFONATE—This salt was prepared according to the method of Barth and Senhofer,[3] save that the sodium salt was obtained through the barium salt instead of the lead salt. The product was dried in a vacuum oven at 140° for 48 hrs. About 800 g. were made and used in all of our fusion experiments. An analysis gave the following results:

(I) 0.1989 g. substance gave 0.1846 g. CO_2 and 0.0302 g. H_2O
(II) 0.2417 g. substance gave 0.2228 g. CO_2 and 0.0358 g. H_2O

(I) 0.5086 g. substance gave 0.2572 g. Na_2SO_4
(II) 0.5005 g. substance gave 0.2532 g. Na_2SO_4

	Found		Calculated for $C_6H_4(SO_3Na)_2$
	I Per cent	II Per cent	Per cent
C	25.31	25.14	25.52
H	1.69	1.60	1.43
S	22.74	22.77	22.73
Na	16.36	16.37	16.30
O (by diff.)	33.90	34.12	34.02

SODIUM HYDROXIDE—This was a good grade of the commercial article (not C. P.), assaying 93.5 per cent NaOH. It was used in powdered form.

APPARATUS—A full description of the apparatus used will be found in the earlier article.[4]

EXPERIMENTAL METHODS

ALKALI FUSIONS—The problem of determining the proper conditions for obtaining the maximum yield of resorcinol resolved itself into a study of the four following factors:

(1) Ratio of sodium hydroxide to sodium benzene *m*-disulfonate.

(2) The proper fusion period.

(3) The proper fusion temperature.

(4) Effect of the addition of water to the sodium hydroxide upon the yield of resorcinol.

Temporarily adopting 310° and 2 hrs. as the proper fusion temperature and period, respectively, and keeping these constant, experiments were conducted in which the ratio of sulfonate to alkali was varied in each tube. At the end of the fusion the tubes were suddenly cooled and analyzed for resorcinol and unused sodium benzene *m*-disulfonate. To determine the proper fusion period, all six tubes were filled with the same amount of alkali and sodium benzene *m*-disulfonate, the two constituents being in the proportion found in the previous experiment to give the best yield of resorcinol, and the fusion again conducted at 310°. At certain intervals of time a tube was removed, suddenly cooled, and analyzed as before. Using the optimum conditions as to period of fusion and ratio of alkali to benzene *m*-disulfonate, experiments were then conducted at different temperatures. The effect of the addition of water to the fusion mixture upon the yield of resorcinol was determined in a similar manner by adding a known amount of water to each tube, under the optimum conditions of the other factors as previously determined.

RESORCINOL DETERMINATION—The cold fused mass was removed from the tube with hot water, filtered, and the filtrate concentrated on the steam bath. It was made up to 200 cc. in a volumetric flask (Solution A), and 50 cc. were measured out with a pipet and transferred to a separatory funnel. It was made distinctly acid with hydrochloric acid, and extracted with five 50-cc. portions of ether, shaking vigorously with each portion for about one minute. The ether was evaporated off at room temperature, with the aid of a small blast of air, the residue dissolved in 200 cc. of water, and an aliquot part analyzed for resorcinol, according to the method of Pence.[1] It was found preferable to standardize the bromine solution against specially purified resorcinol instead of making the standard solution as recommended by the author. The weight of resorcinol was expressed as per cent of the theory.

DETERMINATION OF THE UNUSED SODIUM BENZENE *m*-DISULFONATE—An aliquot part of Solution A (50 cc.) was acidified with hydrochloric acid, diluted with water, boiled until all of the sulfur dioxide had been expelled, neutralized with sodium hydroxide, filtered, and made up to 200 cc. in a volumetric flask (Solution B). An aliquot part (50 cc.) of this solution was transferred to a weighed beaker, evaporated to dryness, dried for 48 hrs. in a vacuum oven at 140°, and weighed. A sample of the residue was analyzed for sulfur, using the Parr fusion bomb for carrying out the sodium peroxide fusion. Another measured portion of Solution B was analyzed for sulfate sulfur by precipitating as barium sulfate with barium chloride in the usual manner. The total sulfur in Solution B found by this determination was deducted from that found by the sodium peroxide fusion, and the result calculated as $C_6H_4(SO_3Na)_2$. The weight of salt thus found was expressed as per cent of the weight of sodium benzene *m*-disulfonate taken for the experiment.

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[1] *Dingler's polytech. J.*, **263** (1887), 154.

[2] *Z. Chem. Ind.*, **2** (1887), 1.

[3] *Ber.*, 8 (1875), 1477.

[4] *Loc. cit.*

[1] THIS JOURNAL, **3** (1911), 820.

EXPERIMENTAL DATA

EFFECT OF AMOUNT OF SODIUM HYDROXIDE UPON YIELD OF RESORCINOL—The results of the experiments in which the amount of sodium hydroxide was made the only variable are shown in Table I and graphically in Fig. 1.

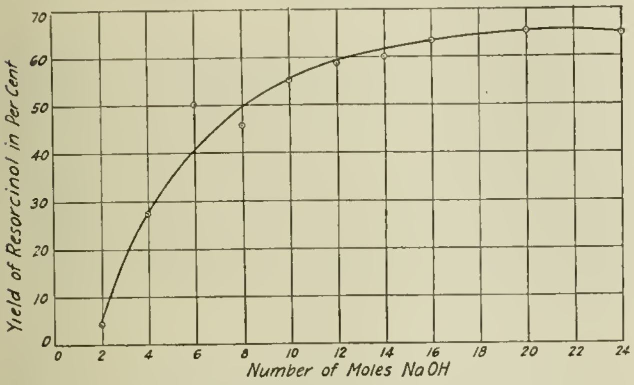

FIG. 1—CONCENTRATION, YIELD CURVE

TABLE I—EFFECT OF VARYING AMOUNT OF SODIUM HYOROXIDE[1]

No.	Ratio $C_6H_4(SO_3Na)_2$: NaOH Moles	Yield of Resorcinol Grams	Yield of Resorcinol Per cent	$C_6H_4(SO_3Na)_2$ Found Grams	$C_6H_4(SO_3Na)_2$ Found Per cent
1	1 : 2	0.2397	4.3	8.0450	57.0
2	1 : 4	1.5183	27.6	4.0702	28.8
3	1 : 6	2.7641	50.2	2.4533	17.4
4	1 : 8	2.5290	45.9	1.3473	9.6
5	1 : 10	3.0560	55.5	1.2367	8.7
6	1 : 12	3.2349	58.8	1.2023	8.5
7	1 . 14	3.3080	60.1	1.2607	9.0
8	1 : 16	3.4950	63.5	1.1675	8.3
9	1 : 20	3.6088	65.6	1.1367	8.0
10	1 : 24	3.5763	65.0	1.0692	7.6

[1] 14.1 g. (0.05 mole) of sulfonate were used in each experiment. Fusion temperature 310° C. Time of fusion 2 hrs.

The table shows that a rather large excess of sodium hydroxide over that required by the theory is necessary for the best yields of resorcinol, which were obtained when from 20 to 24 moles of sodium hydroxide to 1 mole of sodium benzene *m*-disulfonate were used. However, it is also evident that almost as good yields were obtained with 14 to 16 moles of sodium hydroxide, and in subsequent fusion experiments the ratio of 1 mole of sodium benzene *m*-disulfonate to 16 of sodium hydroxide was used.

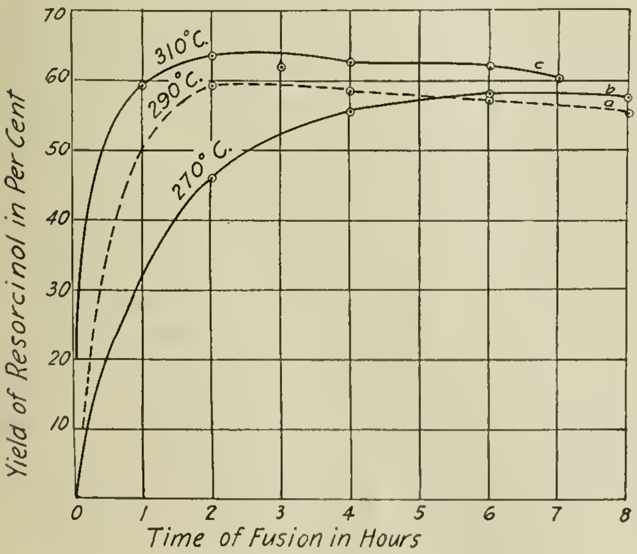

FIG. 2—FUSION PERIOD, YIELD CURVES

EFFECT OF TIME OF FUSION ON RESORCINOL YIELD—The results obtained with fusion periods of 1, 2, 3, 4, 6, and 7 hrs. are shown in Table II, and graphically in Fig. 2, Curve *c*.

TABLE II—EFFECT OF VARYING FUSION PERIOD[1]

No.	Time of Fusion Hrs.	Yield of Resorcinol Grams	Yield of Resorcinol Per cent	$C_6H_4(SO_3Na)_2$ Found Grams	$C_6H_4(SO_3Na)_2$ Found Per cent
1	1	3.2674	59.4	1.2114	8.6
2	2	3.4950	63.5	1.1675	8.3
3	3	3.4143	62.0	1.0099	7.2
4	4	3.4462	62.6	1.1497	8.1
5	6	3.4137	62.0	1.0914	7.7
6	7	3.3162	60.3	1.0511	7.5

[1] Ratio $C_6H_4(SO_3Na)_2$: NaOH = 1 : 16 (0.05 mole : 0.8 mole). Fusion temperature 310° C.

This table indicates that the maximum yield of resorcinol was obtained when the fusion was conducted for 2 hrs. A longer fusion period seems not only unnecessary but also quite undesirable.

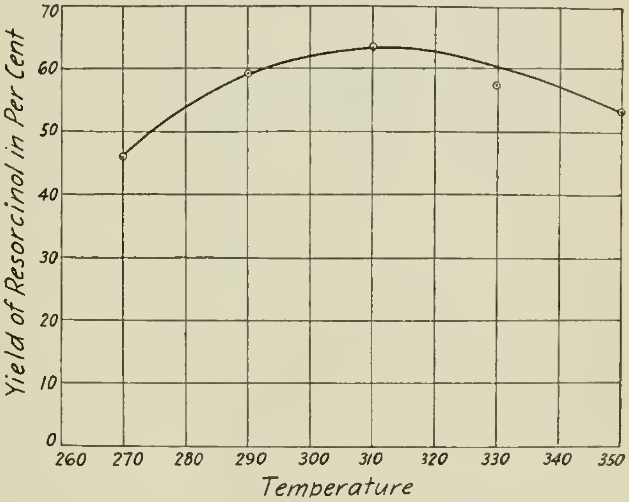

FIG. 3—FUSION TEMPERATURE, YIELD CURVE

EFFECT OF THE TEMPERATURE OF FUSION ON YIELD OF RESORCINOL—The results of fusions at temperatures of 330°, 350°, 290°, and 270° C. are recorded in Table III, and shown graphically in Fig. 3.

TABLE III—EFFECT OF VARYING TEMPERATURE[1]

No.	Temp. of Fusion ° C.	Yield of Resorcinol Grams	Yield of Resorcinol Per cent	$C_6H_4(SO_3Na)_2$ Found Grams	$C_6H_4(SO_3Na)_2$ Found Per cent
1	330	3.1293	57.6	1.0030	7.1
2	350	2.9341	53.3	1.1850	8.4
3	270	2.5296	46.0	3.0807	21.9
4	290	3.2637	59.3	1.5501	11.0

[1] Ratio $C_6H_4(SO_3Na)_2$: NaOH = 1 : 16. Fusion period 2 hrs.

It appears from these results that 310° is the best fusion temperature. At 330° and 350° some destruction of resorcinol must have taken place, since the amount of unused sodium benzene *m*-disulfonate present was about the same or even less than that found in the fusion experiment conducted at 310°. At 290° and 270° the lower yields were due to the fact that the reaction had not gone to completion, as indicated by the somewhat higher per cent of sodium benzene *m*-disulfonate present in the fusion mixture, especially in the one where the fusion was conducted at 270°.

Since the results of the previous experiments showed considerable reduction in the yield of resorcinol when the fusion was conducted for 2 hrs. at temperatures below 310°, it was thought that by increasing the fusion period a corresponding increase in the yield of resorcinol might be obtained. Accordingly, the tubes were charged with the amount of sodium benzene *m*-disulfonate and sodium hydroxide used in the previous experiments, and the mixture fused at 270°. At the end of 4, 6, and 8 hrs., respectively, a tube was removed, suddenly cooled with water, and analyzed. An identical experiment was carried out at 290° and the results obtained are given in Table IV, and graphically in Fig. 2, Curves *a* and *b*.

TABLE IV—EFFECT OF VARYING FUSION PERIOD AT 270° AND 290° C.[1]

No.	Temp. of Fusion ° C.	Yield of Resorcinol Grams	Yield of Resorcinol Per cent	$C_6H_4(SO_3Na)_2$ Found Grams	$C_6H_4(SO_3Na)_2$ Found Per cent
1	270	2.5296	46.0	3.0807	21.9
2	270	3.0675	55.7	1.9470	13.8
3	270	3.1983	58.1	1.4950	10.6
4	270	3.1820	57.9	1.3950	9.9
5	290	3.2637	59.3	1.5501	11.0
6	290	3.2311	58.7	1.3477	9.5
7	290	3.1443	57.1	1.3242	9.4
8	290	3.0560	55.5	1.3261	9.5

[1] Ratio $C_6H_4(SO_3Na)_2$: NaOH = 1 : 16. Fusion period 2 hrs.

It appears from this table that even with longer fusion periods the yields, although improved, are not quite as good as those obtained at 310°. It is, therefore, reasonable to conclude that 310° is the optimum fusion temperature.

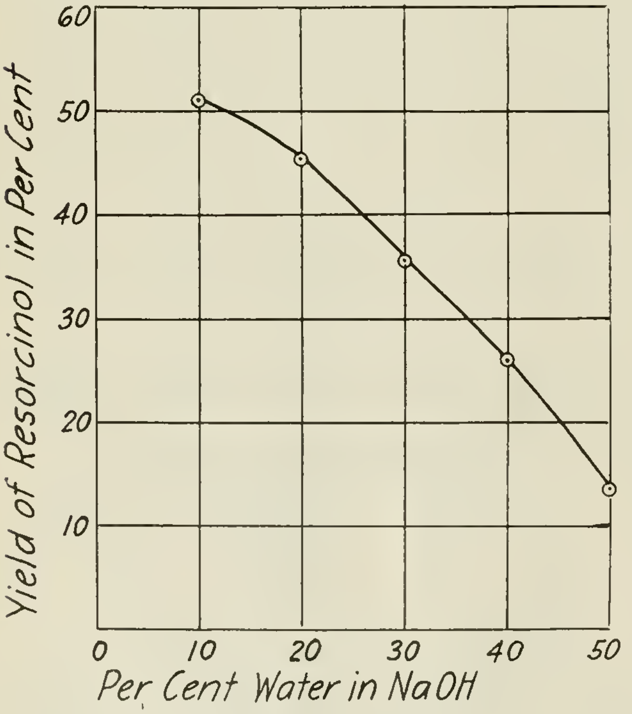

FIG. 4—CONCENTRATION OF WATER AS RELATED TO RESORCINOL YIELD

EFFECT OF WATER IN THE CHARGE UPON THE RESORCINOL YIELD—Since it is a common practice in making alkali fusions of aromatic sulfonic acids to add water to the sodium hydroxide, in order to make the melt less viscid and, therefore, more easily discharged from the fusion kettle, it was considered very important to study the effect of the presence of water upon the yield of resorcinol. The results of experiments in which the amount of water was the only variable are given in Table V and graphically in Fig. 4.

TABLE V—EFFECT OF VARYING AMOUNT OF WATER[1]

No.	Amount of Water Added Per cent of Total NaOH Used	Yield of Resorcinol Grams	Yield of Resorcinol Per cent	$C_6H_4(SO_3Na)_2$ Found Grams	$C_6H_4(SO_3Na)_2$ Found Per cent
1	10	2.8057	51.0	1.3279	9.4
2	20	2.4908	45.3	1.2600	9.0
3	30	1.9632	35.6	1.2182	8.7
4	40	1.4315	26.0	1.4470	10.2
5	50	0.7525	13.7	1.9765	14.0

[1] Ratio $C_6H_4(SO_3Na)_2$: NaOH = 1 : 16. Temperature 310° C. Fusion period 2 hrs.

It is evident that water tends to cut down the yield of resorcinol. In conducting an alkali fusion of sodium benzene *m*-disulfonate for the production of resorcinol no water should be added, although judging from the nature of the curve from 2 to 4 per cent of water would not greatly reduce the yield. Our results on the effect of water bear out the statement of Binschedler and Busch[1] that the fusion must be conducted with the addition of as "little water as possible."

SUMMARY

Using an apparatus especially designed for carrying out of alkali fusions of aromatic sulfonic acids, a study was made of the various factors affecting the fusion of sodium benzene *m*-disulfonate with sodium hydroxide for the production of resorcinol, including temperature, time, ratio of sodium hydroxide to sodium benzene *m*-disulfonate, and concentration of water in the fusion mixture. The results indicate that 310° is the best fusion temperature, 2 hrs. the best fusion period, 14 to 16 moles of sodium hydroxide to 1 mole of sodium benzene *m*-disulfonate the best fusion mixture, and that water tends to reduce the yield of resorcinol.

THE PREVENTION OF SUGAR DETERIORATION BY THE USE OF SUPERHEATED STEAM IN CENTRIFUGALS

By **Nicholas Kopeloff**

LOUISIANA SUGAR EXPERIMENT STATION, NEW ORLEANS, LA

Received June 11, 1920

The deterioration of manufactured cane sugar has been the subject of considerable investigation to which reference has already been made.[2] Following a study of the most important single group of microorganisms, the molds, responsible for sugar deterioration, the writer prepared a chart whereby it was possible to predict the keeping quality of a sugar.[3] It remained to devise some means of eliminating the causative organisms in order to prevent sugar deterioration. Shorey[4] and others have suggested the use of superheated steam in the centrifugals, but so far as we have been able to ascertain no controlled experiments have been conducted to test out the efficiency of such an agent. Unfortunately, it was not possible to arrange for an equipment in our sugar house and mill which would permit of such a study, and it was due to Assistant Director W. G. Taggart, who devised an apparatus to be used in the laboratory centrifugal, that the present experiment was made possible.

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[1] *Loc. cit.*

[2] Kopeloff and Kopeloff, Louisiana Experiment Station, *Bulletin* **166** (1919).

[3] Louisiana Experiment Station, *Bulletin* **170** (1920).

[4] *J. Soc. Chem. Ind.*, **17** (1898), 555.

The centrifugal used was an 11-in., 1915 model, No. 2, made by the International Instrument Company of Cambridge, Mass. The jacket had a diameter of 11 in. and a depth of 3.5 in. A larger concave trough 15.25 in. in diameter and 6.5 in. deep caught the molasses. The device used for superheated steam was simple in construction, consisting of a half-inch intake pipe with two arms (3/8 in. diameter), one inside the basket, stopping 1.5 in. from the bottom, the other between the basket and the trough. These were made of copper, sealed off at the lower end, and had a slit in the side facing the surface of the sugar. The device was securely attached by means of screws to the outside trough. An autoclave was used as a source of steam, the outlet pipe being connected by a nipple and thick rubber tubing with a 10-in. superheater (or heating spiral such as used with an Abbé refractometer), which in turn was connected with rubber tubing to the device in the centrifugal through a hole in the cover, the latter being kept closed during the course of the experiment. Fig. 1 is a diagrammatic illustration of the apparatus used.

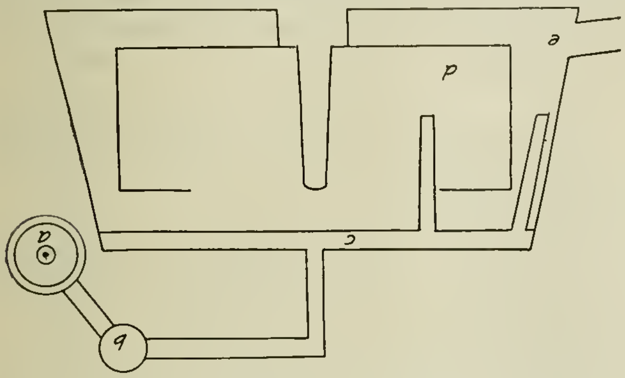

Fig. 1—Diagram of Device for Using Superheated Steam in Laboratory Centrifugal

a—autoclave; *b*—superheater; *c*—intake pipe with arms for delivering steam on inside and outside of basket; *d*—basket; *e*—jacket

Confectioners' crystals, which are large in size, were sterilized and coated with a blackstrap molasses which was heavily inoculated with microörganisms such as *Aspergillus* Sydowi Bainier, *Aspergillus niger*, *Penicillium expansum*, *B. vulgatus*, *B. megatherium*, *B. mesentericus*, and all the bacterial colonies developing from 150 plates poured from Cuban raw sugar. A massecuite of medium density was prepared and the centrifugal steamed out after receiving a swabbing with alcohol containing carbolic acid.

The procedure was then as follows: The autoclave was run up to 22 lbs. pressure or a temperature of 263° F. The massecuite was heated to 104° F. (40° C.) for about 10 min., and poured into the centrifugal basket until it formed a layer three-fourths of an inch deep. The superheater was started with a Bunsen burner (asbestos being used to protect the rubber tubing) to get it well heated before the steam was added, then the centrifugal was put in operation (attaining a maximum of 3,000 r. p. m.) and the steam turned on for 3 min.

Upon stopping the steam and centrifugal the temperature of the sugar was 155° F. (68° C.). Naturally, the sugar cooled very rapidly and doubtless the heat attained while the superheated steam was being applied was considerably in excess of this figure. The sugar was washed as white if not whiter than with a jet of water such as is ordinarily used. Samples of the sugar and the molasses coming from it were taken in sterile containers for bacteriological analysis.

The same procedure was repeated with a 1.5 in. layer of massecuite previously heated to 136° F. (58° C.) for about 5 min. and at about 122° F. (50° C.) for 10 min. more. In this case the steam treatment was interrupted owing to a bend in the tubing which blew off one of the connections. At the end of the treatment the temperature of the sugar was 158° F. (70° C.).

The samples taken above were plated out in three dilutions on Kopeloff's agar,[1] incubated at 30° C., and read after 3 and 7 days. The data are presented in Table I, in which are recorded the closely agreeing averages of quadruplicate determinations of each of the three dilutions.

Table I—Effect of Superheated Steam in the Centrifugal on Number of Microörganisms in Sugar

Treatment	Bacteria Per Gram	Molds Per Gram	Per cent Reductions	
			Bacteria	Molds
Untreated, 40° C.	1,500,000	550	...	...
Steamed	8,000	10	99.47	98.28
Molasses	235,000	275	84.34	50.00
Untreated, 58° C.	200,000	110	...	...
Steamed[1]	14,000	10	93.00	90.91

[1] Steam treatment interrupted.

It will readily be seen that in the first instance the untreated massecuite had 1,500,000 bacteria and 550 molds per g., while the treatment with superheated steam resulted in reducing the content to 8,000 bacteria and 10 molds per g., a diminution of 99.47 per cent of the bacteria and 98.28 per cent of the molds, respectively.

This means an efficiency in the decimation of the microörganisms which is remarkable and the significance of which will be discussed in detail presently.

The molasses from this sugar had 235,000 bacteria and 275 molds per g., a reduction in 84.34 per cent of the bacteria and 50 per cent of the molds.

This is again proof of the sterilizing effect of superheated steam, since it may be inferred that the heat attained for the short time necessary to wash the molasses from the sugar was sufficient to kill more than three-fourths of the bacteria and one-half the molds. Furthermore, this is of practical value from the standpoint of the keeping quality of the molasses. We have previously referred to the unsanitary conditions under which most molasses is kept, frequently in tanks literally covered with a mat of mold mycelium. It is logical to suppose that where the original mass infection may be so materially reduced, the keeping quality of such a product may be greatly enhanced. Moreover, we have here an advantageous substitute for wash water which is frequently of questionable character and often responsible for a heavy inoculation with microörganisms.

Moreover, these data indicate that by far the larger proportion of microörganisms contained in the massecuite leave the centrifugal in the wash. Therefore, when it is the practice to separate the molasses and the wash, a less contaminated molasses is procured with undoubtedly improved keeping quality.

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[1] *Loc. cit.*

In this connection a digression may be permitted, which may be worthy of trial: namely, where molasses is not fermented and it is desired to keep it for some time, we would suggest the use of a thin layer of oil on the surface. This would prevent a mass infection at that vulnerable point and could be easily removed. The oil in this way need not affect either the quality, odor, or taste of the molasses. On the other hand, where mold growth already covers the surface it might be advisable to spray with toluene, which is cheap enough to be economical, germicidal enough to kill the molds, and volatile enough to be removed within a few days by exposure to the air. Since the pressure of time does not permit of the opportunity of developing these suggestions in the sugar mill, they are advanced for what they may be worth.

Returning to the latter half of Table I, it will be seen that where the massecuite was heated to 122° F. (50° C.) the untreated sample contains only about one-eighth the number of bacteria and one-fifth the number of molds present in the massecuite heated to 104° F. (40° C.). This means that a partial sterilization has already been effected. The treatment with superheated steam was interrupted and the final results show that 93 per cent of the bacteria and 91 per cent of the molds were eliminated. It was to be expected that these figures would be somewhat below those obtained in the first instance, since the partial sterilization referred to probably eliminated the least resistant organisms and left a flora relatively more resistant than the one originally present. The interruption of the steam treatment must have been responsible for some loss in efficiency. Finally, the difference may be ascribed to the fact that the layer of sugar in this instance was twice as thick as that used in the first instance. It is to be expected that four important factors would be operating in such an experiment, *viz.*, temperature of steam, duration of application, thickness of layer of massecuite, and speed of centrifugal.

From the data set forth it is evident that the use of superheated steam under the conditions of the experiment was instrumental in almost entirely eliminating the microörganisms present, the important consideration being that this was accomplished without increasing the moisture content of the sugar perceptibly, as in washing with water. As a matter of fact, under mill conditions it might be anticipated that even better results might be obtained where higher temperatures might be so readily available. The procedure has the merits of

(1) Simplicity in construction and operation.

(2) Economy in equipment, installation, and operation.

(3) Efficiency under all conditions.

(4) Yielding a cleaner wash.

In working out a chart for predicting the keeping quality of sugar it was shown that two factors, moisture ratio and degree of infection,[1] operated simultaneously. It is obvious, therefore, that such a striking reduction in mass infection can be effected by the use of superheated steam in the centrifugals that the keeping quality may be greatly enhanced even where the moisture is somewhat more than it should be. For example, a sugar having a moisture ratio of 0.08 will deteriorate when 10,000 to 100,000 mold spores per gram are present. A reduction of 98 per cent, however, bringing the content down to about 1,000 spores per gram would make this sugar safe even though the moisture ratio increased to as much as 0.14 to 0.16.

Thus it may be said that in the investigations on sugar deterioration carried forward in this laboratory, the study of the microörganisms and their activities, which made possible the prediction of the keeping quality of sugars, has found its logical completion in the development of an adequate means for eliminating the microörganisms and consequently preventing sugar deterioration. However, it must be emphasized again that the sugar must be properly handled under sanitary conditions with a minimum possibility of absorbing moisture in order to ensure its safe keeping, since, under optimum conditions, the microörganisms soon propagate rapidly enough to become detrimental.

SUMMARY

1—A simple, economical, and efficient method has been developed for employing superheated steam in laboratory centrifugals.

2—By means of this treatment the bacterial content of sugar has been reduced 93 to 99.5 per cent, and the number of mold spores has been reduced 92 to 98 per cent. The microörganisms in molasses are reduced similarly to a lesser extent.

3—This elimination of microörganisms improves the keeping quality of the sugar as well as the molasses.

4—With superheated steam treatment, the practice of separating molasses and wash results in a considerable reduction of microörganisms in molasses, with consequent improvement in its keeping quality.

THE CAUSE AND PREVENTION OF AFTER-CORROSION ON THE BORES OF FIREARMS[2,3]

By Wilbert J. Huff

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During the past war the Bureau of Mines was requested to investigate the causes of the after-corrosion which sometimes appears on the oiled bore surfaces of firearms subsequent to the use of high-pressure smokeless powders.[4] Experimentation had hardly begun when the armistice was signed, but because of the importance of the problem and the wide general interest attached to it, both in war and peace, it was deemed advisable to continue the study. The Ordnance Department states that more rifles are ruined by improper preparation for storage than from any other cause,[1] and the problem, though primarily military, touches the interest of every owner of a firearm.

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[1] *Loc. cit.*

[2] Published by permission of the Director, U. S. Bureau of Mines.

[3] Read before the Section of Physical Chemistry at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

[4] Although this study was undertaken primarily in an advisory capacity, this Bureau is interested in the problems of corrosion as a part of its work for the preservation and proper utilization of our mineral resources.

THEORIES OF CORROSION

Generally, this corrosion under oil has been attributed to acid explosion products, such as acid nitrocellulose residues, or acids from the primer, or to diffusing acid gases.

CORROSIVE POWDER RESIDUES—Probably those theories which entail the presence of nitric residues on the bore surface preponderate. Thus Guttmann[2] states:

> Most smokeless powders do not leave any residue worth speaking of and the barrels are perfectly clean after a shot, but after using they must be carefully cleaned, because traces of nitric compounds always remain which, combined with the action of the moisture in the air, will attack the barrel and rifling.

Such opinions have led to the compounding of a large number of special and patented preparations seeking to neutralize the residue with alkali or to dissolve it by special organic preparations.[3,4] Substantially, the Ordnance Department advances such a theory as the justification for the use of the concentrated sodium carbonate solution.[6]

Black powder is considered advantageous because it does not leave such a corrosive residue.[6]

POWDER GAS OCCLUSION THEORY—Corrosion effects are sometimes observed for weeks or months after use in spite of repeated swabbing and oiling. This phenomenon suggests a "leaking or sweating-out" process and has inspired a theory which attributes after-corrosion to acid gases from the decomposition of nitrocellulose and nitroglycerin powders. These gases are supposed to be driven by the pressure of explosion into the pores of the metal while it is heated by the exotherm of explosion and the friction of the bullet; upon cooling, they slowly diffuse to the surface and there cause corrosion.[7]

In a book upon rifles and ammunition, Ommundsen and Robinson[6] hold that some acid products are forced into the steel beneath the surface and that violent rusting begins immediately after the discharge of the piece. They recommend the use of abrasive and alkaline greases.

CORROSION FROM THE PRIMER. NON-CORROSIVE PRIMING COMPOSITIONS—Since 1900 the patent literature records a number of attempts to diminish or prevent after-corrosion by the use of various priming mixtures.[1] The theories involved have been various and conflicting.

Some compositions were designed to produce an alkaline residue which would take up the acids assumed to be formed. One employed chromates[2] to give a protective coating on the gun barrel. Another[3] composition contained no oxygen. Halogens were thought to produce acid and so were eliminated,[4] although some retained potassium chlorate in certain of their non-corrosive priming compositions.[5]

Marshall[6] states that potassium chlorate forms chloride which causes the barrel to rust. He does not state whether other ingredients produce corrosive or acid residues or not.

Whelen[7] held that the primer produces corrosive acid. He thought nitrocellulose residues were in themselves harmless but that they mechanically interfered with the cleaning process. He recommended several cleaning agents, among which was a mixture of amyl acetate, acetone, and oil—all non-solvents for potassium chloride.

EMPIRICAL OBSERVATIONS OF PRACTICAL RIFLE MEN—A compilation of the observations of a number of practical riflemen only added to the confusion of these conflicting opinions. Some had never encountered after-corrosion under oil. Others invariably encountered it save when cupro-nickel was removed. Some thought after-corrosion could be eliminated by rubbing the nose of the bullet with a heavy lubricant. Many testified to the "leaking" effects subsequent to cleaning.

EXPERIMENTAL

RIFLES, AMMUNITION, OIL, AND EQUIPMENT—Four U. S. infantry rifles, two of the model of 1903, and two of the model of 1917, were employed. To duplicate service conditions they were used as received, without special treatment. The ammunition was the standard service cartridges primed with typical fulminate, sulfocyanide, and sulfur compositions from various sources. No qualitative differences were ever noted in the corrosive effects of ammunition from these sources.

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[1] Ordnance Department, "Descriptions and Rules for the Management of U. S. Rifle Caliber 0.30 Model of 1917," p. 45. Government Printing Office, **1918**

[2] "The Manufacture of Explosives," Vol. II, p. 274. London, **1895.**

[3] The Beck patents: U. S. Patent 719,074, Jan. 27, 1903; Brit. Patent 15,078 (1901); Austrian Patent 9,766; Wild, U. S. Patent 768,835, Aug. 30, 1904; Klever, U. S. Patent 919,884, April 27, 1909; Brit. Patent 27,254 (1905); Ger. Patents 174,906 and 204,906; Fr. Patent 360,960 (1906); Braun and the Saponia-Werke Ferdinand Boehm, U. S. Patent 862,305, Aug. 6, 1907; Austrian Patent 32,643; Brit. Patent 25,976 (1905).

[4] A large number of "nitro-solvents" are used in the United States. In connection with this investigation a number of such solvents and gun oils have been analyzed by the Petroleum Section of this Bureau. The results will be given in another communication.

[5] Ordnance Manual, *Loc. cit.*, p. 43.

[6] Marshall, "Explosives, Their Manufacture, Properties, Tests, and Uses," **1915** Ed., p. 61.

[7] Pasdach, *Kriegstechnische Z.*, **9**, 1906 (from a translation by H. E. Fleischner); Pauling, Fr. Patent 409,569.

[8] "Rifles and Ammunition and Rifle Shooting," Funk and Wagnalls Co., **1915**, p. 282.

[1] H. Zeigler, Ger. Patent 122,389 (1900); Brit. Patent 14,583 (1900); Austrian Patent 7,074 (1901). (From "Initial-explosivestoff" Escales and Stettbacher, Leipzig, Veit and Co., 1917, pp. 369–370, also pp. 7 and 331–333.) Westfalische-Anhaltische Sprengstoff-aktien Gesellschaft, Ger. Patent 176,719; Fr. Patent 348,721; Lang, Ger. Patent 209,812; Ernest Goodwin and Eley Bros., Brit. Patent 2,682 (1911); U. S. Patent 1,029,287 (1912); Meyer, Brit. Patents 21,337 (1911), 23,493 (1911), 25,550 (1912); Claessen and the Rheinisch-Westfalisch Sprengstoff-akt. Ges., Ger. Patent 277,566 (1915); Fr. Patent 455,369; Buell, U. S. Patent 1,308,393.

[2] Westfalische-Anhaltische Sprengstoff-akt.-Ges., Ger. Patent 176,719; Fr. Patent, 348,721.

[3] Lang, Ger. Patent 209,812.

[4] O. Mertens, *Z. ges. Schiess-Sprengstoffw.*, **9** (1914), 70.

[5] Westfalische-Anhaltische Sprengstoff-akt.-Ges., Ger. Patent 176,719; Fr. Patent 348,721; Claessen and the Rheinisch-Westfalisch Sprengstoff-akt-Ges., Fr. Patent 455,369.

[6] *Loc. cit.*, pp. 61, 426.

[7] "The American Rifle," Century Co., **1918**, p. 599

The oil employed was a widely known brand of light oil having the following composition:[1]

	Per cent
Animal oil (possibly prime lard oil)	52.50
Mineral oil (34° Bé. neutral oil, frequently used as a spindle oil)	47.50
Free acid (probably oleic acid in the animal oil)	1.32

This will hereafter be denominated "Oil A." As this oil gave excellent protection against atmospheric corrosion and practically none against after-corrosion, these properties rendered it very useful for the purpose of the study.

To control the humidities to which the fired rifles were exposed, two wooden cases lined with galvanized iron and supplied with snugly fitting covers were designed as humidors. Each could hold comfortably four fully assembled rifles, placed so that the barrels lay horizontal. The bottom of each case was covered with glass photographic trays which served as containers for the salt or solutions used to control the humidity.

PRELIMINARY EXPERIMENTS—A number of preliminary firing tests were made, using many hundred rounds of service ammunition. The rifles were then carefully swabbed out with cloth and Oil A. Upon exposure to an indoor atmosphere during several winter months no after-corrosion appeared.

TABLE I

DATE	RIFLE	HUMIDITY	REMARKS
May 14	A		Forty rounds were expended in each rifle, the bores were then swabbed with Oil A, and exposed over calcium chloride
May 28	A B	Zero	No corrosion
June 5	A B		No corrosion

Rifles used without change in the next firing test (Table IV)

TABLE II

DATE	RIFLE	HUMIDITY	REMARKS
May 14	C D	Approx. 50 per cent	Forty rounds were expeoded in each rifle, the bores were then swabbed with Oil A, and exposed over 44 per cent sulfuric acid
May 23	C D		No corrosion
June 5	C D		No corrosion

Rifles used without change in the next firing test (Table III)

FIRING TESTS AT KNOWN HUMIDITIES—The first tests (Tables I and II) were carried out as follows: The rifles, without previous treatment, were fired until forty rounds had been expended in each. Each bore was then swabbed with cloth and Oil A until it appeared bright and the swabs were no longer discolored. A generous coating of oil was allowed to remain on the bore. Over the trays in one humidor was spread anhydrous calcium chloride to give a humidity of approximately zero, while into the trays of the other was poured a 44 per cent solution of sulfuric acid to give a humidity of approximately 50 per cent. The rifles were hung in place, two in each humidor. No after-corrosion appeared, although they were allowed to remain under these conditions for 22 days. The rifles were then employed in the tests of Tables III and IV. To obtain the humidity of approximately 100 per cent pure water was substituted for the calcium chloride.

TABLE III

Days after Washing with Sodium Carbonate Solution	DATE	RIFLE	HUMIDITY Per cent	REMARKS
	June 6	C D	Atmospheric	100 rounds were expended in each rifle, and the bores were then swabbed with Oil A
	June 7	C D	100	Rifles placed in the humidor containing pure water
	June 9	C D	100	Bores of both rifles were heavily corroded, although all other metal parts were bright and unattacked. Cold saturated sodium carbonate solution was pumped up and down through each a few times, followed by water and dry patches. Finally rifles were oiled with Oil A and re-exposed
First	June 10	C D	100	A trace of corrosion was found in each bore. This was wiped off with a cloth swab and Oil A. The rifles were then re-exposed
Second	June 11	C D	100	No corrosion
Seventh	June 16	C D	100	No corrosion
Ninth	June 18	C D	100	No corrosion
Eleventh	June 20	C D	100	No corrosion
Fourteenth	June 23	C D	100	No corrosion
				On June 23 both rifles were treated with metal fouling solution.[1] This gave a deep blue, showing the presence of cupro-nickel

[1] Ammonium persulfate.................... 28 g. (1 oz.)
Ammonium carbonate.................... 13 g. (200 g.)
Ammonium hydroxide (28 per cent)........ 177 cc. (6 oz.)
Water.................................... 118 cc. (4 oz.)
(Ordnance Manual, *Loc. cit.*, p. 45)

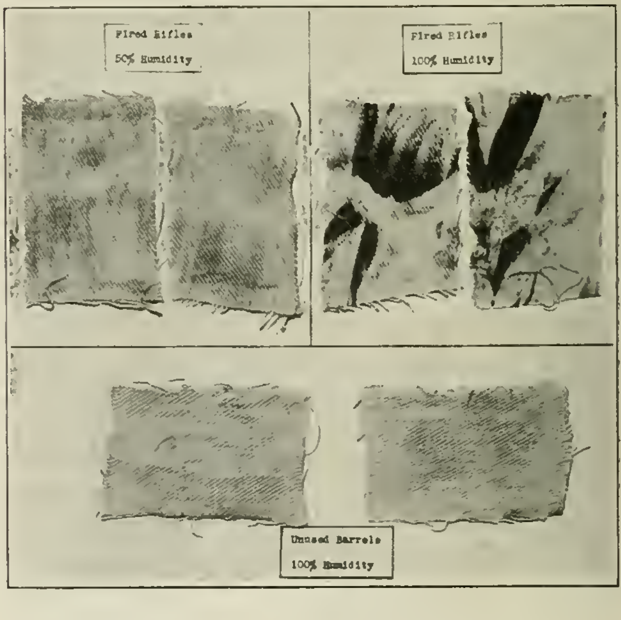

FIG. 1

Table V shows that the corrosion was after-corrosion, which evidently requires a humidity greater than approximately 50 per cent. Fig. 1 also shows this clearly. The swabs photographed are those of June 9, Tables III, IV, and V. Fig. 2 shows the successive first swabs from one of the rifles of Table III. The legends "First Day," etc., designate the day on which the swab was obtained, reckoned from the date on which the sodium carbonate was used. The corresponding swabs from the other rifles were similar in appearance with those shown. Fig. 3 shows the appearance of the swabs from one of the rifles of Table IV. The legends "Third Day—50 per cent Humidity,"

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[1] The above analysis was made by Mr. N. A. C. Smith, of the Petroleum Section of the Pittsburgh Station of the Bureau of Mines.

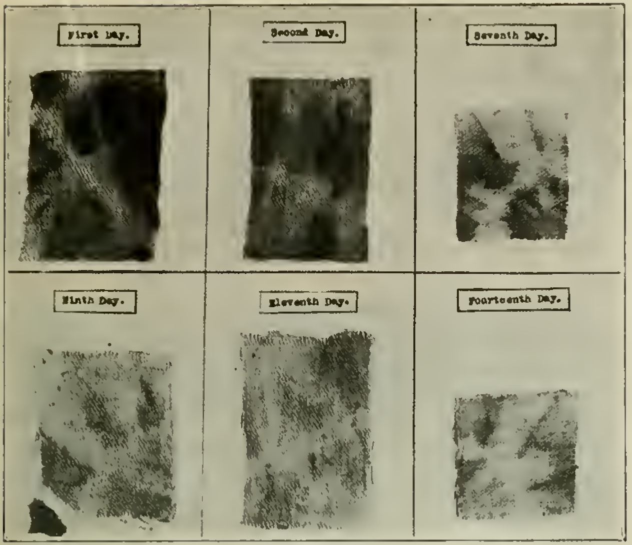

Fig. 2—Swabs from the Tests of Table III

etc., show the relations between humidity and the length of exposure.

Table IV

Days after Exposure	Date	Rifle	Humidity Per cent	Remarks
	June 6	A B	Atmospheric	100 rounds were expended in each, and the bores were then swabbed with Oil A
	June 7	A B	50	The rifles were placed in the humidor containing 44 per cent sulfuric acid
Second	June 9	A B	50	No corrosion
Third	June 10	A B	50	No corrosion
Ninth	June 16	A B	50	No corrosion. Both rifles were transferred to humidor containing water
Days after Transfer to 100 Per cent Humidity				
Second	June 18	A B	100	Heavy corrosion in the bores of both. All other parts bright. Bores were swabbed clean with cloth and oil and re-exposed
Fourth	June 20	A B	100	Continued corrosion in the bores of both rifles, less than that noted on June 18
Seventh	June 23	A B	100	No corrosion. On June 23 both rifles were cleaned using the metal fouling solution. In both the colorless solution turned to a very dark blue, showing the presence of cupro-nickel fouling

Table V—New Barrels, Never Fired

Date	Humidity	Remarks
June 7	100 per cent	Both barrels were coated with Oil A and exposed
June 9		No corrosion
June 10		No corrosion
June 16		No corrosion
June 18		No corrosion
June 20		No corrosion
June 23		No corrosion

CUPRO-NICKEL FOULING NOT CAUSE OF AFTER-CORROSION—In these plates it will be noted that the fired rifles gave some color to all of the patches. When marked "no corrosion" this color was a light green. Tested with potassium ferrocyanide and acetic acid, this green gave the mahogany-brown of copper ferrocyanide. The detached corner of the swab marked "Ninth Day," Fig. 2, was tested in this manner. The metal-fouling solution used on June 23 likewise showed that cupro-nickel fouling was present throughout the tests. As rifles C and D, Table III, had ceased to corrode after June 10, there is no apparent connection between the cupro-nickel fouling and after-corrosion.

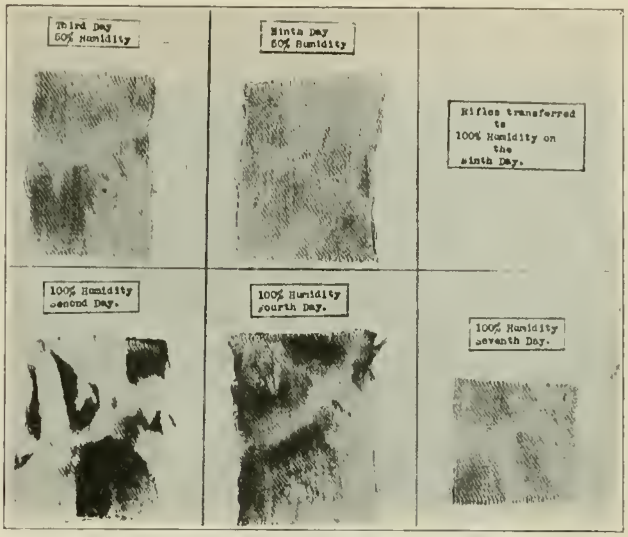
Third Day 60% Humidity
Ninth Day 60% Humidity
Rifles transferred to 100% Humidity on the Ninth Day.
100% Humidity second Day.
100% Humidity fourth Day.
100% Humidity seventh Day.

Fig. 3—Swabs from the Tests of Table IV

This was tested further as follows: Two new barrels, freed from grease, were fouled by driving through each, by mechanical means, five bullets removed from service cartridges. With each succeeding bullet, the driving grew more difficult. In one barrel, the jacket of the fifth bullet struck; further driving carried out most of the lead core, leaving the cupro-nickel jacket about half-way down the bore. Since it undoubtedly made metallic contact with the steel it was allowed to remain. To increase the amount of cupro-nickel present, filings from jackets were thrown into the bores. The whole was coated with Oil A and exposed to 100 per cent humidity. No corrosion developed in either barrel.

NO EVIDENCE OF GAS DIFFUSION—The observations recorded in Tables III and IV contradict Pasdach's theory of diffusing acid gases. Corrosion once initiated proceeded rapidly for a few days only, then ceased. Moreover, while rifles A, B, C, and D were fired on the same date (June 6), two of them (C and D) had ceased to corrode by June 11. According to the gas diffusion theory, all the corrosive gas had therefore passed out from the steel. Rifles A and B were maintained at the same temperature, and it is therefore proper to expect that such gas in their barrels had disappeared, and that in consequence no after-corrosion would appear. However, when exposed to approximately 100 per cent humidity on June 16, both rifles corroded heavily.

Furthermore, the prevention of after-corrosion by the use of certain aqueous solutions, such as the sodium carbonate solution recommended by the Ordnance Department, does not accord with the gas diffusion theory, for it is difficult to conceive how such a solution could penetrate beneath the surface of the steel and remove gases previously dissolved or occluded there.

Again, this gas theory fails to explain the pitting action of the after-corrosion. If the steel acts as a solvent, one may expect the attack of the diffusing acid gases to take place over the entire surface. Examination of corroded bore sections, however, shows centers of corrosion completely surrounded by bright metal. This is illustrated by Fig. 4.

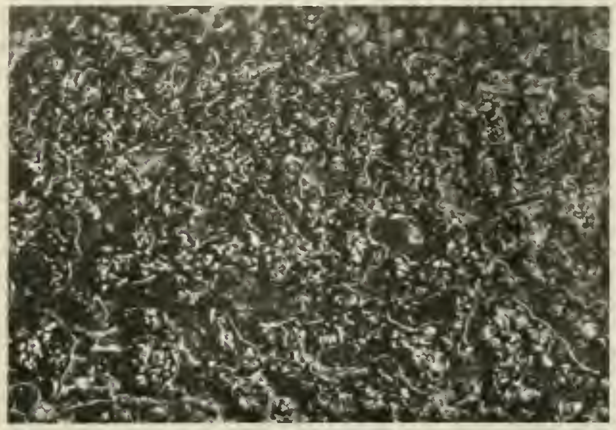

Fig. 4—Photomicrograph Showing Characteristic After-Corrosion beneath an Oil Film

Moreover, the contention that corrosive acid gases are produced by the explosive decomposition of the nitrocellulose under high pressures is contrary to the testimony of a number of investigators of high standing.[1] Carbon dioxide is the only acid gas produced. In the corrosion of iron and steel, this has been shown to play only an unimportant role or none at all.[2]

The gases of explosion also contain a large portion of hydrogen and carbon monoxide. This, coupled with the fact that they have cooled from a very high temperature, renders the presence of oxides of nitrogen impossible.[3]

This also eliminates possible nitrogen oxides from the primer. Among the other possible gaseous products from the primer are hydrogen sulfide from the sulfur, and nitrogen and carbon monoxide from mercury fulminate (if present). An inorganic nitrate, such as potassium nitrate, gives the carbonate, nitrogen, and water. Potassium chlorate loses oxygen and gives the chloride, a neutral salt.

ACID RESIDUES ON BORE SURFACE—Although we are thus obliged to dismiss the "acid gas" theory, those theories which predicate a surface residue which may furnish acid are not so improbable. Thus partly burned nitrocellulose may be lodged on the bore. The slow decomposition of this under atmospheric conditions is known to furnish very corrosive oxides of nitrogen.

To ascertain whether such residues do exist, rifles were fouled by firing forty rounds of service cartridges in each. The bores were then treated with ammonia, or with dilute potassium hydroxide. The solutions thus obtained were examined for nitrate and nitrite, using hydrogen peroxide and the phenoldisulfonic acid method of Chamot, Pratt and Redfield.[1] Neither was found. The bores, however, failed to corrode under oil, showing that the corrosive residue had been removed.

Another fouled rifle was tested for acid by treatment with ammonia, followed by evaporation on a water bath. The residue was nesslerized. No fixed ammonia was found, thus proving the absence of any acid whose ammonium salt is stable under these conditions.

Since these aqueous alkaline solutions do not chemically combine with and remove acid, their valuable property here probably lies in a physical solvent action.

POTASSIUM CHLORIDE—THE CORROSIVE FOULING—Accordingly the examination of the water-soluble fouling was made. The only material found was potassium chloride from decomposition of the chlorate.

A priming composition containing silver permanganate, lead sulfocyanide, antimony sulfide, and trinitrotoluene was then loaded into a number of cartridges, in all other respects similar to the present service cartridge. Rifles were carefully cleaned and rinsed with water to remove any soluble inhibitor of corrosion, then fouled with these cartridges, using ten rounds in one rifle and sixteen in another. After firing, the bores were coated with oil, without unduly disturbing any of the adhering fouling. Exposed to a humidity of approximately 100 per cent for a week, neither rifle corroded.

Ten rounds in another rifle, using cartridges in all respects similar save that potassium chlorate was employed instead of silver permanganate, gave fouling which caused heavy corrosion under oil.

When a steel surface is brightened with emery, coated with potassium chloride crystals, and subsequently with oil, and exposed to approximately 100 per cent humidity with a free access of oxygen, corrosion follows over night.

It is therefore difficult to resist the conclusion that this salt is a cause of the after-corrosion which follows the use of the present service cartridge.

POSSIBLE OBJECTIONS TO THE POTASSIUM CHLORIDE THEORY—Proponents of other explanations may, however, object that this salt should be removed by the mechanical polishing of the bright bore surface; that a coating of potassium chloride fails to explain the corrosion following repeated cleanings over long intervals of time; that it fails to explain the light sweating which sometimes follows the use of the sodium carbonate solution;[2] and that it fails to explain the severity of after-corrosion and its continuance under conditions in which unoiled steel surfaces do not undergo atmospheric corrosion. Further it may be suggested that the wide use and many endorsements of non-aqueous nitro-solvents and gun oils controvert this explanation, or that the after-corrosion experienced in the arid regions of Arizona and the Sahara does not accord with the experimental findings reported above.

It may be shown, however, that all of these confusing points are in no way at variance with the conclusion that potassium chloride is the sole corrosive fouling deposited by the explosion of the present service cartridges.

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[1] A. Noble, *Phil. Trans.*, **205** (1905), 207; A. Brynk, "Properties of Powders and Their Action in Closed Chambers and in Cannon," trans. from the Russian by Bernadou, Washington, Government Printing Office, **1904**, p. 46; Sarrau and Vielle, *Mem. poudr. Salp.*, **2** (1884–5), 126, 337; from Brunswig (Eng. Ed. of Munroe and Kibler), p. 164–5.

[2] Cushman and Gardner, "The Corrosion and Preservation of Iron and Steel," New York, **1910**, p. 38; Dunstan, Jowett and Goulding, *J. Chem. Soc.*, **87** (1905), 1548.

[3] According to the Ordnance Department, the mean temperature of the gases throughout the bore during the explosion of the present service cartridge is about 2150° C. (3900° F.); cf. Noble, *Loc. cit.*

[1] *J. Am. Chem. Soc.*, **33** (1911), 382.

[2] Ordnance Manual, *Loc. cit.*, p. 44.

FAILURE OF MECHANICAL CLEANING PROCESSES

Fig. 5 is a photomicrograph[1] showing the characteristic tool wounds and fissures upon the bore surface of a new barrel.[2] The depth and number of these fissures are no doubt much greater on old surfaces which have been subject to neglect.

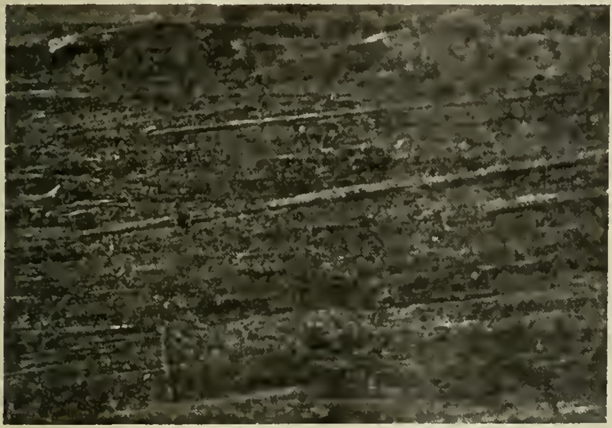

Fig 5—Photomicrograph Showing Characteristic Fissure on the Bore Surface of a New Barrel

The potassium chloride is deposited over the surface and lodged within the fissures. Mechanical swabbing from the breech fills the fissures and so renders the salt invisible to inspection from the muzzle or breech.

Fig. 5 is a weighty argument against those cleaning processes which endeavor to remove the corrosive fouling by abrasives.[3]

SWEATING, AND OCCURRENCE AND RECURRENCE OF CORROSION OVER LONG PERIODS OF TIME

The puzzling "leaking-out" effects which are evidenced by the occurrence and recurrence of corrosion after cleaning and by "sweating" are quite as simply explained.

The preceding experiments have shown that high humidities are a necessary factor in after-corrosion. When the atmospheric conditions are such that these humidities are attained, water vapor "leaks in" to the corrosive fouling already present on the surface and corrosion results. Subsequent mechanical swabbing, which may entail the use of an oil in which potassium chloride is not soluble, may remove a portion of this salt and rust, while the remainder is rubbed into the surface pits and fissures where it is invisible to inspection. Here it remains inactive until local atmospheric conditions are such that the requisite high humidity is again attained, when the process is repeated. Since the time interval involved between periods of high atmospheric humidity is indeterminate, it is not surprising that weeks or months may be involved. On the other hand, an extended period of high humidity may furnish sufficient water vapor to develop the maximum corrosion and to dissolve completely the potassium chloride, so that subsequent swabbing would carry out with the rust most or all of the corrosive fouling. This explains the rapid cessation of corrosion in the experiments of Tables III and IV.

"Sweating out" has been attributed to the action of acid fouling sealed under metal fouling and therefore inaccessible to cleaning agents.[1] This explanation cannot, however, be completely correct, for such metal fouling, if tightly sealed, would likewise prevent water vapor from reaching the corrosive fouling. This last must therefore remain inactive. Obviously, the fouling which causes "sweating" must be in communication with the outside atmosphere.

Since the chloride is driven into the fissures by enormous pressures, and since it can be removed only by the action of a suitable solvent whose action may be delayed by insoluble[2] fouling at the mouth of the fissure, it is only to be expected that a hasty swabbing with an aqueous solution will fail to completely remove all the corrosive fouling from the most inaccessible pits. In that event, subsequent exposure to high humidities will be followed by a light corrosion or "sweating." The obvious remedy is to prolong the cleaning process sufficiently.[3] Acting upon this assumption, the writer has never since encountered "sweating out" following the use of aqueous cleansing agents.

AFTER-CORROSION AT HUMIDITIES BELOW SATURATION

The evidence so far presented has shown that after-corrosion proceeds at humidities of approximately 100 per cent but not at humidities of approximately 50 per cent. For the complete explanation of some of the phenomena encountered in after-corrosion, it was, however, necessary to determine the humidity relations somewhat more closely.

This was done by fouling a rifle[4] with fifty service cartridges. The barrel was then sawed into sections and exposed under oil to various humidities above saturated solutions of single C. P. salts in equilibrium with the solid phase. The temperatures were maintained constant at 30° C. by immersion in a thermostat.[5]

Corrosion occurred above a saturated solution of sodium chloride but did not occur above a saturated solution of calcium nitrate.

Parallel experiments, using sections of a rifle barrel which had never been fired and C. P. potassium chloride, gave identical results.

Marshall[6] gives the following values for humidities which may be obtained by such saturated solutions:

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[1] Figs. 4 and 5 were made by Dr. R. Thiessen and Mr. G. L. Henneman, of the Pittsburgh Station of this Bureau.

[2] This was taken near the muzzle and should, therefore, represent the best portion of the bore surface.

[3] Compare H. Ommundsen and E. H. Robinson, *Loc. cit.*

[1] Ordnance Manual, *Loc. cit.*, p. 44.

[2] Possibly, though not necessarily, metal fouling.

[3] The use of aqueous ammonium persulfate solutions for the removal of metal fouling here also prolongs the solution process and so prevents "sweating out."

[4] Previously cleaned with sodium carbonate and ammonium persulfate solutions

[5] Every precaution was taken to prevent condensation. The salts and solution were placed in the thermostat a number of days before the sections were exposed, and immediately before exposure each section was warmed to a temperature above 30° C.

[6] *Loc. cit.*, p. 341.

	Temperature ° C.	Relative Humidity
Sodium chloride	15	76
Calcium nitrate	18	62

The values are not exact and do not apply to temperatures other than those stated. They do represent approximately the humidities obtained, however, and because local temperature differences, variable impurities in the constituents of the explosives, and variable surface conditions on the bore all affect the exact humidity at which after-corrosion begins, highly exact estimations would probably not enable one to predict possible humidity relations with very great accuracy.

It is evident, therefore, that although after-corrosion requires high humidities, these humidities are well below the dew point (100 per cent humidity).

MECHANISM OF AFTER-CORROSION

Students of corrosion have generally recognized that liquid films are indispensable.[1] On pure, brightly polished steel, water vapor does not form a liquid film until the dew point is reached.[2] Potassium chloride, however, deliquesces at humidities below saturation and forms a corrosive liquid film in direct contact with the metal beneath the oil film.[3]

Since potassium chloride solutions do not corrode iron and steel in the absence of oxygen,[4] this element is also an essential factor in after-corrosion.

SEVERITY OF AFTER-CORROSION AND ITS CONTINUANCE UNDER CONDITIONS IN WHICH UNOILED STEEL SURFACES DO NOT UNDERGO CORROSION

Since under atmospheric conditions the necessary humidity for the potassium chloride-liquid film is reached more readily and maintained much longer than the dew point at which cleaned iron and steel rusts, after-corrosion proceeds more rapidly than the ordinary atmospheric corrosion of cleaned steel surfaces.

Alkali chlorides are popularly considered very corrosive, although experimental evidence has been presented to show that saturated solutions of such chlorides at all temperatures are less corrosive than pure water,[5] and that at certain temperatures all concentrations are less corrosive.[6] This popular conception probably rests largely on their ability to form corrosive liquid films at humidities below saturation.

AFTER-CORROSION IN ARID REGIONS

Nothing here presented contradicts the testimony of riflemen who have encountered after-corrosion in the desert regions of Arizona or on the sands of the Sahara, for while such regions are arid, and the humidities at noon day relatively low, the coming of night is accompanied by a rapid cooling of the earth's surface. Thus, although the absolute water content of the atmosphere may not change materially, the drop in temperature may be, and often is, so great that precipitation of dew takes place. In certain desert regions, such dew forms an important part of the water supply of the inhabitants. Special reports furnished the writer from stations of the U. S. Weather Bureau in the arid regions of Arizona, Utah, and Nevada showed that all of these stations have observed the formation of dew.

POSSIBLE ABSENCE OF AFTER-CORROSION IN HIGH ATMOSPHERIC HUMIDITIES

Since the humidity relations involved depend only upon the temperature of the bore surface and the absolute water content of the atmosphere, a bore surface maintained at a temperature well above the atmospheric temperature will never rust. Thus the maximum water vapor possible in an atmosphere of 15° C. (59° F.) corresponds to a partial pressure of 17.2 g. per sq. cm. Should the bore surface be at 25° C. (77° F.), water upon this would possess a partial pressure of 32 g. per sq. cm., consequently the maximum relative humidity possible on the surface at equilibrium is less than 55 per cent when referred to the temperature of the bore surface, and no after-corrosion can result. Such humidity relations explain decreased corrosion during the winter and when stored at warm places indoors.

PREVENTION OF AFTER-CORROSION

With the information now available it is possible to prescribe simple methods for preventing after-corrosion.

EXCLUSION OF WATER VAPOR—One method consists in excluding water vapor. This may be done by tightly stopping both ends of the bore as soon as convenient after firing.

Greases and oils differ in their ability to transmit water vapor and oxygen, but both do transmit these and are in consequence unsuitable for this purpose.[1]

SOLUTION AND REMOVAL OF POTASSIUM CHLORIDE—As already shown, the value of the sodium carbonate solution and of the ammonium hydroxide solution depends upon their water content, since this dissolves the potassium chloride.

When such solutions are not available, water alone may be used. When possible, this is best applied by placing the muzzle of the barrel in a receptacle containing water, preferably hot. From the breech, a rod and swab is then used as a piston to pump the water thoroughly over all portions of the bore surface. This treatment should be continued for several minutes, after which the bore should be treated further to remove cupro-nickel fouling, or, if preferred, polished with dry swabs and oiled.

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[1] Dunstan, Jowett and Goulding, *Trans. Chem. Soc.*, **1905**, 1554; Friend, "The Corrosion of Iron and Steel," Longmans, Green and Co., **1911**, pp. 17–18.

[2] Howe, "Metallurgy of Steel," 2nd Ed., **1** (1891), 96.

[3] The evidence cited indicates that after-corrosion proceeds at a humidity somewhat lower than that at which pure potassium chloride deliquesces. However, this may be caused by traces of impurities such as sodium chloride in the corrosive fouling. The humidity necessary for corrosion is also less when capillary surfaces are involved. Friend, *Loc. cit.*, p. 96; W. Thorton Murray, *J. Iron and Steel Institute*, **1** (1910), 703. It was predicted that a more deliquescent chloride would cause corrosion at even lower humidities. Sections from an unfired barrel coated with calcium chloride, then Oil A, corroded above the saturated solution of calcium nitrate.

[4] Friend, *Loc. cit.*, p. 142.

[5] Adie, *Min. Proc. Inst. Civil Engineers*, **4** (1845), 323; from Friend. *Loc. cit.*, p. 140.

[6] Friend, *Loc. cit.*, p. 139.

[1] The protective action of oils against ordinary atmospheric corrosion depends upon certain relations involving the surface energies of the liquid water and oil. A preferential coating of the steel by the oil prevents the contact between the steel and the *liquid* water.

It may be that the sodium carbonate and the ammonia solutions possess some value as detergents for the removal of insoluble fouling. Detergent properties can be supplied by soap, a reagent universally available.

Corrosion tests on rifles fouled with service cartridges, then cleaned with water alone, or with soap and water, showed that such treatment completely prevented after-corrosion.

The statement by the Ordnance Department that the sodium carbonate solution must be at least 20 per cent in strength[1] is clearly not correct, at least in so far as it applies to the removal of the corrosive residue from the present ball service cartridges, and while there appears to be no objection to the continued use of this solution, it is not indispensable.

NON-AQUEOUS "NITRO-SOLVENTS" AND "GUN-OILS"—There seems to be a deep-seated prejudice on the part of practical riflemen against the use of water and aqueous solutions on firearms. Other cleaning agents, non-aqueous, and variously denominated as "powder solvents," "nitro-solvents," and "gun-oils," have been recommended. A number of these have been analyzed under the direction of Dr. E. W. Dean of the Petroleum Section of the Bureau, and submitted to firing tests by the writer. In general, they may contain an oil or lard, blended with various organic solvents of nitrocellulose, such as acetone and amyl acetate. None of these ingredients are solvents for potassium chloride, and consequently many of the mixtures possess no anti-corrosive properties. The use of these, because it induces a false sense of security, is not only unwise but even dangerous. If, after the use of such a mixture, the rifle is maintained at a low humidity, no corrosion will result. Therein appears to lie the true explanation for the supposed value of such mixtures and for much of the confusion which has surrounded the problem of after-corrosion.

There does, however, appear to exist a class of mixtures which, while they do not contain a solvent for potassium chloride, nevertheless possess some value as anti-corrosives. These mixtures contain, among other things, oil, and a certain peptizing agent, such as ammonium oleate. Exposed under certain conditions, these mixtures appear to form an emulsion with water from the aqueous vapor in the atmosphere. A probable explanation of their action is the solution of the potassium chloride in the aqueous phase of this emulsion, while corrosion is diminished or inhibited by the protective coating of the metal by the oil phase or the colloid. The exact mechanism of this action is not, however, clear, and the whole presents a problem worth further study. The emulsions and emulsifying oils tested gave partial but not complete protection against after-corrosion.

TEST FOR USEFUL SOLVENTS

To determine whether a solvent is useful or not without exposing a valuable firearm to corrosion, a soft steel plate may be brightened with emery paper and coated with potassium chloride. The oil or solvent should be used as directed, taking especial care, however, not to dislodge mechanically the salt from direct contact with the steel. The whole should then be placed in a large covered container where it is exposed to humidity above a fairly large surface of pure water for not less than a week. Only those processes which give complete protection should be employed on the bore of the firearm.

THE ADDITION OF AN INHIBITOR OF CORROSION. BLACK POWDER RESIDUES—The various patented alkaline greases and pastes designed to be left in the gun barrel owe their value not to the neutralization of acid, but to the property of inhibiting corrosion which many alkalies possess.

The non-corrosive properties said to be possessed by black powder residues apparently depend upon a large percentage of potassium carbonate formed from the decomposition of the nitrate.[1,2]

The writer has prepared a simple and cheap inhibiting paste by gelatinizing a strong solution of sodium carbonate with soap. This may be used to furnish a preliminary protection in the field. The best results are obtained when it is subsequently removed by water. It is an excellent detergent, possesses many of the properties of the sodium carbonate solution, and may be readily transported and handled.

NON-CORROSIVE PRIMING COMPOSITIONS—The simplest remedy for after-corrosion consists in the use of cartridges which do not deposit a corrosive fouling. In the present service cartridge this requires the elimination of only one ingredient, the potassium chlorate of the primer. The substitute must be one which upon explosive decomposition shall yield either a residue insoluble in water or a residue whose solution in water does not corrode steel. In practice, only compounds containing halogen must be avoided. Nevertheless, the proper elimination of the chlorate presents a problem of no mean magnitude. The priming composition is one of the most vital of the cartridge parts, and the universal use of potassium chlorate is an excellent testimonial of its value.

Non-corrosive primers are at present under investigation by the Bureau of Mines. While some very promising preliminary results have been obtained, it is as yet too early to make positive recommendations.

AFTER-CORROSION FROM LOW-PRESSURE NITROCELLULOSE POWDERS

Initially, the scope of the investigation described on the foregoing pages was limited to the study of that corrosion which follows the use of the present high-pressure service cartridge and the foregoing discussion has dealt only with this corrosion.

With cartridges generating lower pressures, the incomplete combustion of the nitrocellulose to corrosive acid products is much more probable. While it was not possible to make a complete study of this point, a few tests with non-corrosive priming compositions and a low-pressure nitrocellulose powder have shown that corrosion from the nitrocellulose powder probably occurs only with extremely low confining pressures, such as those of blank cartridges. No nitrocellulose corrosion followed the use of a low-pressure gallery powder confined behind the full weight 0.30 caliber bullet.

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[1] *Loc. cit.*, p. 45.

[1] The reader interested in the composition of the residues obtained from black powder will find in Guttmann, Vol. I, pp. 336–348, a discussion on this subject and many references to the original literature.

[2] These black powder residues are largely water soluble and may be readily removed by a suitable aqueous medium.

SUMMARY

A review of the scientific, patent, and trade literature, and the compilation of the experiences of many practical riflemen has indicated much confusion in theories dealing with the after-corrosion of firearms and much divergence in the practices recommended for prevention. Generally this corrosion has been attributed to acid products on the bore, although other explanations, including the action of chlorides, have been advanced. A critical laboratory study, comprising the exposure of fired rifles and fouled barrel sections to known humidities, the chemical examination of the corrosive residue, the use of special ammunition, and the analysis and testing of many "nitro-solvents" and other compositions recommended as preventatives showed the following:

The present high-pressure smokeless cartridge leaves no nitrocellulose residue and no corrosive acid residue. After-corrosion following the use of such cartridges is caused by the explosive deposition of a water-soluble salt or salts in whose aqueous solution steel corrodes, together with subsequent exposure to a high humidity and the presence of oxygen. In the present service ammunition this salt is potassium chloride from the decomposition of the chlorate in the primer.

Such water-soluble salts are retained in tool wounds and pits on the bore surfaces in which they cannot be seen from the breech or muzzle, and from which they cannot be removed mechanically. They are easily dissolved by water or suitable aqueous solutions.

After-corrosion may also be prevented by keeping both ends of the bore tightly corked.

The present service ammunition can be rendered non-corrosive by eliminating the chlorate of the primer. It may be possible to develop a non-corrosive primer which will not affect the present ballistic properties of this cartridge. This point is under investigation.

A number of non-aqueous compositions recommended for cleaning firearms possess little or no value. Their supposed virtue apparently rests upon tests conducted at humidities so low that no corrosion could occur.

After-corrosion proceeds below the dew point.

A simple test for differentiating between worthless and valuable cleaning compounds is described.

Corrosion from nitrocellulose powder probably occurs only when the confining pressure is extremely low, as in blank cartridges.

ACKNOWLEDGMENTS

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STRENGTH AND VELOCITY OF DETONATION OF VARIOUS MILITARY EXPLOSIVES[1]

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During the past three years many tests on military explosives have been conducted at the laboratory and at the proving ground of this company. It would not be possible to review in a short paper all the data accumulated. This discussion, therefore, will be limited to the strength, velocity of detonation, and fragmentation tests of some of those military explosives that were used or proposed for use during the war.

STRENGTH

One of the first considerations of a military explosive is that of strength. The delivery of the explosive at the desired point by shell, or other means, is so expensive that it is desirable to have as strong an explosive as possible. Various methods have been proposed and used for determining strength, but the one found most satisfactory is the ballistic mortar, by means of which the various explosives are tested for strength in comparison with a standard explosive whose properties are generally well known. The ballistic mortar used in the author's work is similar to the one described by Comey and Holmes,[2] and its construction and operation are briefly as follows: Length of pendulum, 10 ft.; weight of mortar, 524 lbs.; diameter of explosion chamber, 2 in.; length, 5.5 in.; diameter of shot chamber, 4$^7/_8$ in.; length of shot, 5 in.; weight of shot, 36.5 lbs. Ten grams of TNT are shot in the mortar, followed by that weight of the explosive under test, as found by trial shots, which will deflect the mortar approximately an equal number of ballistic degrees.

Table I

Explosive		TNT Value in Ballistic Mortar Tes
Ammonium nitrate		10.5[1]
Ammonal		
Ammonium nitrate	89.0	11.2
TNT (crude)	6.0	
Al	5.0	
Amatol (hot pressed)		
Ammonium nitrate	80.0	12.1
TNT	20.0	
Amatol (melt).		
Ammonium nitrate	50.0	11.8
TNT	50.0	
Ammonium nitrate	70.0	11.9
TNT	20.0	
TNX(trinitroxylene)	10.0	
Ammonium nitrate	80.0	11.9
Trinitroanisol	20.0	
Ammonium picrate		10.5[1]
Dinitrodichlorobenzene		8.6
Dynamite (50 per cent nitroglycerin)		9.8
Hexanitrodiphenylamine		11.1
Nitrocellulose (13.35–13.50 per cent N)		12.0
Nitroglycerin		14.0
Nitrostarch (12.80 per cent N)		11.4
Picric acid		10.6
Tetranitroaniline (TNA)		12.1
Tetranitromethylaniline (Tetryl)		12.1
Trinitroanisol		10.6
Trinitronaphthalene		8.2
Trinitrotoluene (TNT)		10.0
Trinitroxylene (TNX)		8.8
TNT	60	9.3
TNX	40	

[1] Calculated values: see page 871.

The TNT value of the explosive is obtained by calculation. For example, if it required 11.5 g. of an explosive to deflect the mortar the same number of degrees that 10.0 g. of TNT would deflect it, the TNT value would be $10.0/11.5 \times 10$ or 8.7, and the explosive would be 87 per cent as strong as TNT.

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[1] Presented at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

[2] *8th Intern. Congr. App. Chem.*, **25** (1912), 209.

In Table I are given the TNT values of the most common explosives that were used in the World War. Other explosives are also included in order to give an idea of the relative strengths of explosives with which we are more or less familiar.

The figure for ammonium nitrate was derived by calculation from results obtained when it was substituted in various percentages in dynamite, since ammonium nitrate itself is not sufficiently sensitive to detonation by means of a blasting cap. To make these substitutions trustworthy, it was necessary to maintain an equal excess of oxygen in all the dynamite mixtures. Ammonal was an explosive used in mining and sapping operations, of about the same strength as 60 per cent nitroglycerin dynamite made with active base. Amatol was one of the most important military explosives used in the war, but, since the so-called "melt" amatol was not sensitive enough to detonation with a blasting cap, it was necessary to obtain results on dry mixed materials. Ammonium picrate also was not sensitive enough with blasting cap, and its strength was calculated from substitution in various dynamite mixtures. While not detonating completely with a blasting cap, ammonium picrate when shot in the mortar with a No. 6 cap had a TNT value of 8.24, and when shot with a special tetryl blasting cap had a value of 9.9. The strength of high-grade nitrocellulose is greater than perhaps would be expected, but this material has a very low density, hence its limited application. Nitroglycerin is included to show that it surpasses in strength explosives that are generally regarded as very strong. TNA and tetryl have the same strength, while hexanitrodiphenylamine is intermediate between these explosives and TNT. Although picric acid is stronger than TNT, its use as a military explosive has been limited because of its cost, the large amount of raw materials required for its production, and difficulty in loading. In spite of these objections, it was used to a considerable extent by the French and Italians.

VELOCITY OF DETONATION

A high velocity of detonation is greatly desired in military explosives, especially those that are contained in steel shells, for the reason that, to be effective for a great distance, the fragments from the shell should be animated with a high velocity. Although the chemical constitution of an explosive controls its velocity of detonation, the latter can be altered[1] to a certain extent by varying:

(1) The diameter of the explosive column.

(2) The density to which the explosive is pressed.

(3) The method of confining the charge.

Six explosives, representing material largely used or proposed for use as shell fillers, were tested for velocity of detonation under the following conditions. The explosives were cast or malleted into wrought-iron pipes, 12 in. long, $1^9/_{16}$ in. inside diameter, with $^1/_8$ in. wall thickness. The pipes were open at both ends when the explosive was detonated. A hole, 1 in. in diameter and 2 in. in depth, was drilled in one end of the explosive column. This hole was loaded with 28 g. tetryl in which a No. 6 blasting cap was imbedded, which served as primer and booster in detonating the explosive under test. At distances of 4 and 10 in. from the booster end of the pipe, $^9/_{32}$-in. holes were drilled to take the velocity cap and cordeau as employed in the Dautriche method of testing; and on the opposite side of the iron pipe, $^9/_{32}$-in. holes were drilled 5 and 11 in. from the booster end of the pipe. The purpose of the two sets of holes was to obtain simultaneous velocity records on the one test piece. The velocity figures obtained from the two records were averaged, as it was believed that this would give more trustworthy results.

The method of obtaining the velocity of detonation was that of Dautriche, using detonating fuse, as described by Comey.[1] The velocity of the detonating fuse was accurately determined by means of a recording chronograph of the Mettegang type, and was found to be 5300 m. per sec. The results of tests on six explosives are shown in Table II. TNT sample No. 168, having a melting point of 80.1°, was used in all tests except B, where crude TNT melting at 77.3° was used. The TNX was granular in structure and had a freezing point of 163°. Two samples of ammonium nitrate were used, having the following characteristics:

SAMPLE	AN No. 276	AN No. 279
	Per cent	Per cent
NH_4NO_3 (purity)	99.0	98.1
Granulation		
20–40 mesh	3.4	67.0
40–60	32.6	24.0
60–100	37.0	6.0
100+	27.0	3.0
TOTAL	100.0	100.0

The results in Table II show that TNT gave the highest velocity, and that for shell fillers any one of the six explosives would be satisfactory. The mean variation of velocity is within 200 m./sec., which is probably as near as could be expected by this method, when taking a record on a high velocity explosive on a column only 6 in. in length.

The mean variation of 230 m./sec. for Explosive B, which consisted of a mixture and not a homogeneous compound like Explosive A, is considered very good. It should be noted that crude TNT was used in this mixture, which would give a lower velocity than the refined material.

Explosive C gave a greater variation in velocity figures than might perhaps be expected. This is not attributed to the method so much as to the composition itself. It is well known that in melt amatol, containing only 40 per cent ammonium nitrate, the nitrate has a tendency to settle out of suspension. Since the mixture is not homogeneous the velocity results should be expected to be somewhat erratic.

In Explosive D, the 50 : 50 melt amatol gave very concordant results, which may be accidental, or due to the homogeneity of the mixture. Ammonium nitrate has less tendency to settle out of suspension in 50 : 50 amatol than from mixtures containing less nitrate.

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[1] Marshall, "Explosives," **2** (1917), 482.

[1] *7th Intern. Congr. App. Chem.*, **3b** (1909), 30.

Table II—Velocity of Detonation of Six Explosives

Explosive Composition	A TNT (80.1°)	B TNT (77.3°) 60 TNX (163°) 40	C TNT (80.1°) 60 AN No. 276 40	D TNT (80.1°) 50 AN No. 276 50	E TNT (80.1°) 55 AN No. 279 45	F TNT (80.1°) 20 AN No. 276 80
Density	1.91	1.56	1.59	1.56	1.55	1.40
Velocity, m./sec	7390	6525	7595	7000	7065	5775
	7450	6970	6660	6880	6715	5655
	7960	6920	8125	7235	7920	6135
	7715	7175	7000	7070	6565	5680
	7480	7390	7820	6930	6880	6360
Average	7600	7000	7440	7020	7030	5920
Mean variation	191	230	488	103	371	261

The variable velocity results of Explosive E may be attributed to the settling of the nitrate. The coarse nitrate has more tendency to settle than the fine.

Explosive F, hot pressed amatol, had a mean variation of 261 m./sec., which is considered very good for a mixture.

These velocity figures probably are fairly comparable with those obtained in explosive shells. One important point brought out is that coarse ammonium nitrate does not have any deleterious effect on the velocity of melt amatol, especially if there is 55 per cent TNT present.

To show the effect of density on velocity of detonation, a few tests are recorded on tetryl and TNT. Tetryl, when hand tamped into a 1.25 × 8 in. paper dynamite cartridge shell to a density of 1.0, had a velocity of 5450 m./sec., and, when compressed into pellets, 1.25 in. in diameter and 1 in. long, with a density of 1.40, and these pellets were wrapped in paper, a velocity of 7300 m./sec. was obtained. Since the diameters were equal, the increase of 185 m./sec. must be attributed to an increase of 0.4 in density. TNT when hand tamped into 1.25-in. dynamite cartridges to a density of 1.0, gave a velocity of 4600 m./sec. No figures are available for velocity of TNT compressed into pellets of the same diameter and shot under exactly the same conditions.

FRAGMENTATION TESTS

The brisance of an explosive is usually referred to as its violence or shattering effect, and this characteristic is due to two properties, *viz.*, strength and velocity of detonation, but it is not known exactly how great a value should be given to each when obtaining the value of brisance by calculation. A practical way of determining brisance is by means of fragmenting steel shells filled with explosives, and comparing the fragments with those obtained from a shell loaded with TNT as a standard. Just what constitutes suitable fragmentation is not clearly defined. Naturally, when a shell detonates, it is blown into various sized pieces, some of which are no larger than a pin head, and, as would be expected, these small pieces are not effective, except perhaps to blind a person. For the above reasons pieces of a certain size are arbitrarily considered as effective, and shell fragments are counted on this basis, usually taking TNT as a standard. In our early work on fragmentation it was customary to count the fragments held on a 2-mesh screen, and those passing a 2-mesh screen and held on a 6-mesh screen. As this involved considerable work, a revised method was used, which consisted in counting the fragments held on 2- and on 4-mesh screens. On account of this change in procedure, it will be necessary to give two tables showing the fragmentation of shells containing the explosives shown under velocity of detonation. All the explosives shown in Table II are not given under fragmentation, because it was necessary to use a different kind of shell on some of the tests.

Table III—Fragmentation Tests on 3-In. U. S. Army Base Detonating Shells

Explosive Composition	A TNT (80.1°)	B TNT (76.6°) 60 TNX (167.6°) 40	C TNT (80.1°) 60 AN[1] (No. 277) 40
Density of explosive	1.60	1.56	1.59
Weight of explosive (g.)	449	432	465
Weight of tetryl in fuse (g.)	28.1	28.1	28.1
Weight of shell (grams)	5608	5642	5662
Weight of fuse (grams)	616	616	616
Metal recovered (grams)	6103	6226	6142
Metal recovered (per cent)	98.0	99.4	98.2
Per cent metal recovered			
Held on 2-mesh	56.7	59.9	63.5
Held on 6-mesh	37.4	35.5	32.3
6+	5.9	4.6	4.2
Number of fragments			
Held on 2-mesh	204	179	186
Held on 6-mesh	3087	2824	2558
Total[2]	3291	3003	2744

[1] Fine crystalline ammonium nitrate, 97.5 per cent NH_4NO_3.
[2] Represents average of 5 tests.

The shell chosen for most of our fragmentation work was the U. S. Army 3-in. base detonating shell, fired by means of a medium caliber base detonating fuse. This fuse is very efficient from the standpoint of detonating explosive mixtures, although not from a mechanical point of view. The 3 in. shell was chosen because fragmentation pits will not stand up long under the action of larger shells. The fragmentation pit was cylindrical in shape, 10 ft. in diameter and 11 ft. high, with a concave roof held in place by sand ballast.

Table IV—Fragmentation Tests on 3-In. U. S. Army Base Detonating Shells

Explosive Composition	A TNT (80.0°)	F TNT(80.0°) 20 AN[1] (No. 283-A) 80	G TNT (80.0°) 20 TNX (168°) 10 AN[2] (No. 292) 70
Density of explosive	1.6	1.4	1.5
Weight of explosive (g.)	505	422	454
Weight of tetryl in fuse (g.)	28.0	28.0	28.0
Weight of shell (grams)	5668	5623	5626
Weight of fuse (grams)	616	616	616
Metal recovered (grams)	6090	6100	6181
Metal recovered (per cent)	96.9	97.8	99.0
Per cent metal recovered			
Held on 2-mesh	58.1	70.2	73.8
Held on 4-mesh	33.3	23.9	20.7
Held on 6-mesh	4.1	3.0	2.7
6+	4.5	2.9	2.8
Number of fragments			
Held on 2-mesh	195	193	220
Held on 4-mesh	1495	868	890
Total[3]	1690	1061	1110

[1] 62 per cent passes 60 mesh, 96.8 per cent NH_4NO_3.
[2] 92 per cent passes 60 mesh, 96.0 per cent NH_4NO_3.
[3] Represents average of 5 shots.

On the base of the pit was an anvil on which the shells exploded when dropped through a 4 in. iron pipe entering the top of the pit. The pit was constructed of 1-in. boiler plate reinforced by wooden piles, and had the necessary entrance for workmen, and port holes for the gases to escape. The shell was placed in a cradle on a platform 25 ft. above the pit and armed.

The operator retired behind a barricade and inverted the cradle by pulling a wire, causing the shell to slide down the pipe, where it detonated on the anvil. After the gases resulting from the detonation had been cleared out, workmen swept up the fragments in the pit. The results of the fragmentation tests with various explosives are shown in Tables III and IV. Explosive A, containing TNT alone, gave a greater number of fragments than Explosives B or C. Likewise Explosive B gave more fragments than Explosive C. This is no doubt due to the greater brisance of Explosive B as compared with Explosive C. In Table IV, TNT is shown to be superior to the other two explosives, due to greater brisance. While Explosives F and G are stronger than TNT, the latter has a higher velocity of detonation, and this characteristic seems to overbalance the inferiority in strength, within certain limits. The fragmentation results indicate that any of these explosives would be satisfactory as shell fillers.

SUMMARY

1—The strength of several explosives, used or proposed for military use, is given, as compared with TNT, the comparison being based on the results of the ballistic mortar test.

2—The velocity of detonation of several military explosives has been determined under known conditions of density and confinement.

3—Several military explosives have been detonated in steel shells, and the resulting fragments have been compared as to number and size with those obtained when using TNT as a standard bursting charge.

SOME OBSERVATIONS ON THE DETERMINATION OF CELLULOSE IN WOODS[1]

By S. A. Mahood

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Some time ago the Forest Products Laboratory took up the systematic study of the chemistry of American woods. The results of a preliminary study of the subject were published in 1917 by Schorger.[2] The complex nature of wood from a chemical point of view, together with the scattered and incomplete information on methods, necessitated confining the method of attack to the determination of a number of constants under arbitrary but rather well-defined conditions which would show (1) possible variations in the composition of the different woods, and (2) the presence and percentage of constituents of possible commercial value, in addition to those already known; and which would give data upon which conclusions might be drawn regarding the chemical constituents of wood as a whole.

Since the publication of Schorger's results several contributions to the subject of wood chemistry have been made. Johnsen and Hovey[3] have investigated balsam fir (*Abies balsamea*) and aspen (*Populus tremuloides*) after extraction with ether, alcohol, and water. Schwalbe and Becker[1] have analyzed typical species of German woods and obtained results which on the whole correspond satisfactorily with those of Schorger for similar American woods. König and Becker[2] have examined several European woods particularly for their non-cellulose content. Determination of lignin by four different methods gave surprisingly concordant results. The pentosan-free cellulose values obtained by difference are much lower than those obtained by Schwalbe and Becker using the chlorination method. A proximate analysis of five California woods has been made by Dore.[3]

These contributions, as well as earlier ones, are characterized by the diversity in form of material employed for investigation and also by suggested modifications in methods, apparatus, or procedure, particularly for the determination of cellulose.

Schorger[4] has pointed out that one of the most important points in determining cellulose consists in obtaining the sample in proper physical condition, and Schwalbe[5] has indicated the necessity of further standardizing methods and apparatus for the analysis of all fibrous raw materials. It is the purpose of this paper to give some data, obtained in connection with the analysis of woods, which have a bearing on these two problems.

EXPERIMENTAL[6]

THE EFFECT OF SIZE OF PARTICLE ON YIELD OF CELLULOSE—Wood is exceedingly difficult to disintegrate uniformly, and material in a uniform state of division and composed of particles of rather limited dimensions appears to be of prime importance for the determination of cellulose if comparable results are to be obtained.

In the application of their chlorination method to wood Cross and Bevan[7] state that it should be reduced "to a state of the finest possible division," and suggest the use of a fine plane for this purpose. Dean and Tower[8] found ground wood passing a 24-mesh sieve unsatisfactory, but obtained more suitable material by using a woodworker's rasp and removing the fine particles from the sample by sifting through cheese cloth or a very fine sieve. Sieber and Water[9] used finely rasped wood graded to pass through a No. 75 sieve but not through a No. 110. Schorger used shavings not over 0.005 in. thick from which all particles passing a 40-mesh sieve had been removed. Johnsen and Hovey employed raspings passing an 80-mesh sieve but not a 100-mesh sieve. Dore's samples consisted of "fine sawdust," while Schwalbe and Becker and König and Becker analyzed material in the form of wood flour (holzmehl).

The variations that may be obtained by using material secured by some of the above methods are shown in Table I. The samples of western larch (*Larix occidentalis*) had been extracted for 4 hrs. with a minimum boiling-point mixture of ethyl alcohol and benzene. All values in this and subsequent tables are calculated on an oven-dry (105° C.) basis.

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[1] Read at the Symposium on Cellulose Chemistry at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

[2] This Journal, **9** (1917), 556, 561.

[3] *Paper*, **21** (1917–18), No. 23, 36.

[1] *Z. angew. Chem.*, **32** (1919), 229.

[2] *Ibid.*, **32** (1919), 155.

[3] This Journal, **11** (1919), 556.

[4] *Loc. cit.*, p. 566.

[5] *Z. angew. Chem.*, **31** (1918), 193; *J. Soc. Chem. Ind.*, **37** (1918), 685*a*

[6] Acknowledgment is made to Mr. D. E. Cable for assistance in securing the experimental data given.

[7] "Cellulose," **1903**, 266, 244.

[8] *J. Am. Chem. Soc.*, **29** (1907), 1121, 1125.

[9] *Papierfabrik.*, **11** (1913), 1179; *J. Soc. Chem. Ind.*, **32** (1913), 974

TABLE I

SAMPLE No.	CONDITION OF SAMPLE	Cellulose Per cent
1	Shavings obtained with a cabinetmaker's scraper. Retained on a 40-mesh sieve	54.20
1	Shavings obtained with a plane. Retained on a 40-mesh sieve	55.10
1	Sawdust passing a 40-mesh sieve	50.30
2	Shavings obtained with a cabinetmaker's scraper. Retained on a 40-mesh sieve	58.87
2	Sawdust passing a 40-mesh sieve	54.90

These values were obtained under uniform conditions and are, therefore, comparable, but the cellulose residues were not entirely free from unchanged particles of wood. The variations are due:

(1) To too wide a range in the size of particles in the material used, which causes an attack on the cellulose of the smaller particles before the non-cellulose material can be completely removed from the larger particles.

(2) To a possible fractionation of the material due to sifting out certain portions.

(3) To incomplete extraction of the resinous materials which if not completely removed form a protective coating to some portions of the sample.

To determine the effect of the size of particle on the yield of cellulose the series of determinations given in Table II were made. The material for analysis was obtained by converting the wood first into sawdust and then grinding the sawdust to the various sizes in a disk mill having a shredding effect. Care was taken to avoid fractionation of the material. The ground sawdust was sifted by using the standard testing sieves of the American Society of Civil Engineers. The samples were all extracted for 4 hrs. or more with a minimum boiling-point mixture of benzene and ethyl alcohol prior to chlorination.

TABLE II

SAMPLE No.	SPECIES	Size of Material Mesh	Cellulose Per cent
1	Western larch (*Larix occidentalis*)	40– 60	49.16
		60– 80	50.54
		80–100	52.49
		100–120	51.03
2	Western larch (*Larix occidentalis*)	40– 60	55.05
		60– 80	55.64
		80–100	56.78
		100–120	51.56
3	Eucalyptus (*Eucalyptus globulus*)	40– 60	56.18
		60– 80	56.92
		80–100	59.69
		100–120	59.09

The cellulose obtained in each case was treated with chlorine and sodium sulfite to the point where no color was obtained and the residue was entirely free from unchanged wood particles. The results show a maximum yield of cellulose with material which passes an 80-mesh but is retained on a 100-mesh sieve. This size of material has the further advantage that in contrast to the larger mesh material it is uniformly reduced, and unlike the finer material, gives a product which is easily handled, does not tend to pack, and is readily filtered in the course of the analysis.

Since raspings or shavings have been considered the best forms for wood for an analysis, comparison was made between raspings and material obtained by grinding sawdust. The materials when sifted gave the percentages of different sized material recorded in Table III. The wood used was *Eucalyptus globulus*.

TABLE III

	Raspings		Ground Sawdust	
	Grams	Per cent	Grams	Per cent
Total	94.5	100	167.0	100
Retained on 80-mesh sieve	46.0	48.7	14.3	8.5
80–100 mesh	14.5	15.3	44.1	26.4
Passing 100 mesh	34.0	36.0	108.7	65.1

The ground sawdust gives a larger percentage of material in the desired fraction and is probably more representative, since a larger portion of the wood has been disintegrated to a fineness beyond that desired.

Cellulose determinations on the two samples after extraction with alcohol-benzene gave the following results:

TABLE IV

Per cent Cellulose from	
Raspings	Ground Sawdust
58.31	59.43
58.23	59.59
58.30	59.23
58.64	...

Ground sawdust appears to be as satisfactory as raspings as a form of material for analysis from the standpoint of yield, and is equally as satisfactory from the standpoint of manipulation.

THE CELLULOSE DETERMINATION—The chlorination method of Cross and Bevan continues to be the only method applicable to the determination of cellulose in woods. It has been subjected from time to time to modifications for the purpose of facilitating manipulation and also for the purpose of obtaining a better yield of cellulose or a supposedly purer product. Renker[1] found that a preliminary digestion with one per cent caustic soda was unnecessary and reduced the yield of cellulose. Schorger confirmed this conclusion. Sieber and Walter modified the procedure by allowing the material to remain in the crucible throughout the treatment with chlorine and sodium sulfite. Johnsen and Hovey used this procedure, and recently Dore[2] has employed it in preference to a modification devised by him. Johnsen and Hovey also modify the method by subjecting the wood samples to a preliminary hydrolysis with acetic acid in glycerol at 135° to 140° C.

For the purpose of comparing the two methods of procedure, *i. e.*, chlorination in a beaker in a closed vessel and chlorination in a Gooch crucible, the analyses recorded in Table V were made.

TABLE V

		CELLULOSE Cross and Bevan's Method as Modified by Renker	
SAMPLE	SPECIES	Sieber and Walter's Apparatus	Schorger's Apparatus
1	Western larch	50.97	52.73
1	Western larch	50.82	52.24
2	Western larch	53.51	56.84
2	Western larch	53.23	56.72

The loss in weight due to the action of chlorine on the fibrous pad used in the Gooch crucible was found to be appreciable, giving cellulose values 0.29 per cent too high on the average. A corresponding correction was made in the values given.

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[1] "Bestimmungsmethoden der Cellulose," **1910**, p. 44.

[2] THIS JOURNAL, **12** (1920), 264.

Five one-half hour chlorinations were required for complete reduction following Cross and Bevan's procedure, while periods of 20, 15, 15, 10, and 10 min. were required with the modified procedure. The higher yield obtained using the original procedure, notwithstanding the longer exposure to chlorine, is probably accounted for by a lower concentration of chlorine and a lower chlorination temperature. Cross and Bevan[1] have pointed out that the yield of cellulose can be augmented by allowing the chlorination to proceed at as low a temperature as possible. Renker[2] made his chlorinations at zero.

Johnsen and Hovey obtained yields of cellulose by their modification of the chlorination method which were from 2 to 4 per cent lower than those obtained by the original method. We obtained similar reductions in yield as indicated in Table VI, the wood analyzed being western larch. One of the purposes of the modification is to reduce the furfural-yielding constituents in the cellulose, and the data show a small reduction has been secured.

TABLE VI

		Johnsen and Hovey's Modification		Cross and Bevan's Method as Modified by Renker			
Sample	Constituent Determined	Sieber & Walter's Apparatus Per cent		Sieber & Walter's Apparatus Per cent		Scborger's Apparatus Per cent	
		Ind.	Mean	Ind.	Mean	Ind.	Mean
1	Cellulose	46.18		50.97		52.73	
		46.23	46.21	50.82	50.90	52.24	52.49
2	Cellulose	50.43		53.51		56.84	
		50.48	50.46	53.23	53.37	56.72	56.78
1	Pentosan in cellulose	7.01		7.72		7.75	
		6.76	6.89	7.63	7.68	6.94	7.35
1	Pentosan-free cellulose	...		...		...	
		...	43.03	...	46.99	...	48.64

The figures show that the proposed modification lowers not only the percentage of pentosan or furfural-yielding constituents but also the pentosan-free cellulose. The ratio of loss of pentosan-free cellulose to loss of pentosan is approximately 1 : 2. This does not confirm the statement of those proposing the modification to the effect that the acetic acid-glycerol mixture is "able to hydrolyze the lower carbohydrates and a large portion of the furfural-yielding constituents without attacking the cellulose." Dore[3] in a recent article shows that the more resistant portion of the cellulose, the α-cellulose, is attacked by the acetic acid-glycerol mixture. This modification of the chlorination method appears, therefore, to be of doubtful value, especially since approximately the same result could be attained by a further chlorination of the sample than usual.

SUMMARY

A uniform size of particle is essential if comparable results are to be obtained in the determination of cellulose in woods. Material which passes an 80-mesh standard (American Society of Civil Engineers) sieve but is retained on a 100-mesh sieve has been found to be most satisfactory from the standpoint of both yield and manipulation. Material obtained by a single mechanical process of disintegration may give a sample on sifting which is not representative. To avoid this a combination of two processes, sawing and grinding, has been used.

The procedure recommended by Sieber and Walter for chlorination gives a lower yield of cellulose than the original Cross and Bevan method, probably because of the higher temperature at which chlorination takes place.

The modification of the Cross and Bevan method proposed by Johnsen and Hovey appears to be of doubtful value since the cellulose as well as the hemicelluloses and furfural-yielding constituents are attacked.

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[1] *J. Chem. Soc.*, **41** (1882), 105.

[2] *Loc. cit.*

[3] THIS JOURNAL, **12** (1920), 264.

THE DETERMINATION OF TRUE FREE SULFUR AND THE TRUE COEFFICIENT OF VULCANIZATION IN VULCANIZED RUBBER[1]

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Sulfur in vulcanized rubber has generally been considered as present in two forms, the so-called free and the combined sulfur. It has been realized for some time, however, that sulfur which was called free and hence, implicitly at least, considered available for further vulcanization, did not exist entirely in the elementary form. It is evident that during vulcanization the sulfur will react with other materials present, such as resins, proteins, organic and inorganic accelerators, and fillers. This naturally removes a certain amount of sulfur from active participation in the reaction between rubber and sulfur. All of the inorganic compounds will be insoluble in acetone; hence, unless a correction is made for the sulfur present as sulfide or sulfate, the results on the coefficient of vulcanization will be high. The reaction products of sulfur with the resins, proteins, and organic accelerators may be wholly or partly soluble, or entirely insoluble in acetone, and any of the old methods which did not take into account their formation gave erroneous results for free and combined sulfur.

Furthermore, any compounds formed by the reaction between sulfur, resins, proteins, etc., will, on heating, give up their sulfur in the form of H_2S or some other compound, and never as elemental sulfur. Hence, although the compounds may decompose, no sulfur, once combined, becomes available for further vulcanization unless there is an oxidizing agent present, an extremely rare condition in the vulcanization of rubber. The liberation of sulfur from polysulfide is not considered in this paper. The behavior of accelerators, fillers, etc., is being investigated along the lines laid down, and the work is confined for the present to stocks which are made up of rubber and sulfur only.

It is the object of this paper to present two methods, one for the true free sulfur determination and the other for a more accurate figure for the coefficient of vulcanization than could be obtained by the older methods.

It is evident from the foregoing remarks that the sulfur present in vulcanized rubber may be divided into four parts:

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[1] Paper read before Rubber Division at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

Sulfur soluble in acetone:
- (1) Combined with resins and proteins
- (2) True free sulfur

Sulfur insoluble in acetone:
- (1) Combined with rubber
- (2) Combined with resins and proteins

METHODS FOR DETERMINING TRUE FREE SULFUR

Considering first the sulfur which is soluble in acetone, it is evident that a solvent which would dissolve either the sulfur or the organic material (part of which may contain sulfur of combination) without affecting the other, would solve the problem. Unfortunately, all solvents for either will dissolve both to a greater or less extent. The entire extract very readily dissolves in 95 per cent alcohol. The alcohol will also dissolve about 0.04 g. of sulfur in 100 cc., the amount of sulfur usually obtained in an ordinary analysis. If, however, the extract is treated with alcohol already saturated with sulfur, it will dissolve all of the organic material present but none of the elementary sulfur. The sulfur remains in the flask after the solution is decanted, and can be weighed as such or oxidized and weighed as barium sulfate.

PREPARATION OF SATURATED ALCOHOL—The saturated solution of sulfur in ethyl alcohol, to be referred to as "saturated alcohol," is made by heating an excess of sulfur with the alcohol for about 3 hrs. at 70° to 75° C. and allowing to cool slowly to room temperature. Before used it is allowed to stand at least 24 hrs. in order to insure complete crystallization of the dissolved sulfur. As all later crystallizations are carried out at room temperature a variation of a few degrees in the temperature at which equilibrium is reached does not materially affect the results. As a precaution, however, the solution is kept in contact with solid sulfur to insure saturation at all times.

DETAILS OF METHOD—A one-gram sample of the ground rubber is extracted with acetone for 16 hrs. in an Underwriters' apparatus. The acetone is distilled off, the residue dried at 60° to 65° for half an hour and treated with 50 cc. of saturated 95 per cent alcohol, and the flask and contents weighed. An accuracy of 0.5 g. is sufficient for this weighing. It is then warmed to about 50° C. for a few minutes to insure complete solution of all the organic material and allowed to cool slowly to room temperature. Before it has reached this temperature the flask is again weighed and any alcohol lost during the heating is replaced with pure 95 per cent alcohol. The flask is then well covered and allowed to stand for 24 hrs. to permit the complete crystallization of any of the elementary sulfur of the extract which may have dissolved. The liquid is then carefully decanted, and the residue washed two or three times by decantation with 5 cc. of saturated alcohol and dried. It may then be weighed directly, or oxidized and weighed as $BaSO_4$. It is unnecessary to wash the residue with pure alcohol inasmuch as the amount of sulfur left by the evaporation of the saturated alcohol is very slight. One cc. of 95 per cent alcohol will dissolve only 0.0004 g. of sulfur and it is easily possible to decant the liquid so that not over 0.5 cc. will remain in the flask. The results obtained by this method are given in Table I.

TABLE I

Total Acetone-Soluble Sulfur	Soluble in Acetone but Insoluble in Saturated Alcohol				
	a	*b* (1 Hr.)	*c* (8 Hrs.)	*d* (24 Hrs.)	*e*
3.22	2.17	2.29	2.48	2.69	3.22
3.29	2.17	2.30	..	2.79	3.06
3.22	2.19	..	..	..	3.08
3.24	2.19	..	..	..	2.93
3.28	2.27	..	..	..	..
3.28	2.27	..	..	..	..
3.26	2.28	..	..	..	..
3.22	2.33	..	..	..	..
3.26	2.35	..	..	..	..
3.21	2.39	..	..	..	..
Av, 3.248	2.40	..	..	..	..
	2.42	..	..	..	..
	2.44	..	..	..	..
	2.64	..	..	..	..

DISCUSSION OF RESULTS

The closely checking figures for total free sulfur prove that the acetone extraction was complete and that the method of oxidation with nitric acid plus bromine is suitable for this determination.

For the sulfur insoluble in saturated alcohol the figures vary between 2.17 and 3.22 per cent and have been divided into four classes, according to slight modifications in procedure. The results listed under *a*, varying from 2.17 to 2.64 per cent, were the first obtained. This variation is altogether too great to permit the general use of the method employed. As the theory is sound, there must be some error in manipulation. The first possible place for error is in the control of the temperature of the saturated alcoholic solution of the extract during the crystallization of the sulfur. A control within 2° did not, however, improve the results, that is, the temperature coefficient of the solubility of sulfur in alcohol is less than the other experimental errors. The next point was the rate of crystallization of the sulfur. Solutions of the acetone extract in saturated alcohol were allowed to stand 1, 8, and 24 hrs. before decanting and washing. The figures in Columns *b*, *c*, and *d* show that for accurate results a 24-hr. crystallization is necessary.

As a check on the method, one sample was run by rapidly washing out the organic material of the acetone extract with a very small amount of cold alcohol. A total of about 8 or 10 cc. was used and the entire operation of three washings did not take more than 4 or 5 min. The residual sulfur was oxidized and weighed as barium sulfate, giving 2.81 per cent of true free sulfur, a value which checks with that obtained from the 24-hr. crystallization from saturated 95 per cent alcohol.

The effect of the temperature used for drying the acetone extract before treatment with saturated alcohol was determined by drying four samples at temperatures ranging from 75° to 90° C. The results given in Column *e* vary between 2.93 and 3.22 per cent, showing that at these temperatures some reaction takes place between the sulfur and the resins, forming alcohol-insoluble compounds. The sulfur remaining insoluble in the alcohol from overheated samples is never pure yellow as is that from samples which were dried below 65° C., indicating that if dried at too high a temperature some of the organic material is insoluble in the alcohol. To obtain accurate results the total acetone extract should not be dried at temperatures above 65° C., or for more than half an hour in a well-ventilated oven.

It was decided that if a more dilute alcohol would dissolve all the organic material and less sulfur than the 95 per cent alcohol, the error introduced in case crystallization was incomplete would be smaller. It was found that 100 cc. of 75 per cent alcohol would dissolve only 0.008 g. of sulfur, as compared with 0.040 for the 95 per cent alcohol. The 75 per cent solution also completely dissolved the organic matter in the extract. Upon substituting "saturated" 75 per cent alcohol, the results were 2.80, 2.85, 2.83, 2.84, 2.85, and 2.82, averaging 2.833. In these determinations the solution of resins, etc., in the saturated 75 per cent alcohol was allowed to stand only 3 hrs. to complete the crystallization of the sulfur before decanting and washing.

The results check very well with the 24-hr. crystallization from 95 per cent saturated alcohol, and with the one obtained by quick washing with pure 95 per cent alcohol.

A 24-hr. crystallization from the saturated 75 per cent alcohol yielded the following results: 2.86, 2.84, 2.80, and 2.79, averaging 2.823.

The most concordant results are evidently obtained from 75 per cent alcohol. Their correctness is established by the checks obtained with the different methods.

	Per cent
24-hr. crystallization from saturated 95 per cent alcohol	2.74
Rapid wash with 95 per cent alcohol	2.81
3-hr. crystallization from saturated 75 per cent alcohol	2.83
24-hr. crystallization from saturated 75 per cent alcohol	2.82

The figure thus obtained is the value of the true free or elemental sulfur which is available for further vulcanization of the rubber. The remainder of the acetone-soluble sulfur is combined with resins, etc., and does not participate in further vulcanization.

COEFFICIENT OF VULCANIZATION

The combined sulfur in rubber stocks has been considered to be the sulfur which was not extractable with acetone. In case inorganic sulfides were present a correction was made. As stated above, however, it is possible that some of this sulfur may be combined with resins and proteins in acetone-insoluble compounds. Hence, a method whereby the residual sulfur could be determined after these compounds had been separated from the rubber would give a much better value for the coefficient of vulcanization.

It has been shown[1] that about 85 per cent of the resin of Hevea rubber is saponifiable. Such being the case it is probable that part at least of any resin-sulfur compounds which are insoluble in acetone would also be saponifiable and rendered soluble in alcoholic potash. The protein matter will also be hydrolyzed and some of these products will dissolve in the alcoholic solution. In any case any sulfur extracted by this method will not be sulfur which has been combined with the rubber. The many failures to remove the combined sulfur by any means substantiate this view. The experiments of Spence[2] show that all of the free sulfur is extracted by acetone in about 8 hrs., and hence it is probable that a 16-hr. extraction will remove every trace of it.

A few experiments showed that from the stock used to determine the true free sulfur, alcoholic potash would remove an additional 0.30 to 0.35 per cent of sulfur. In order to show that this was not due to the removal of sulfur combined with the rubber or to the disintegration of the sample, successive extractions were run on the same piece. Two 4-hr. extractions removed all the sulfur, absolutely no precipitate of barium sulfate being obtained when the third and fourth extracts were oxidized and treated with barium chloride.

DETAILS OF METHOD—A one-gram sample of ground rubber is extracted 16 hrs. with acetone and the residue dried. It is then boiled for 8 hrs. with 75 cc. of a 5 per cent alcoholic potash solution and washed once or twice with hot alcohol. As the removal of the last traces of alkali is very difficult the sample is extracted 16 hrs. (over night) with alcohol in an Underwriters' apparatus. The solutions are then mixed and the alcohol distilled off. The residue is oxidized first with 15 cc. of a solution of bromine in potassium bromide (120 g. KBr and 160 g. Br_2 in 1 liter of water) in order to prevent the violent action of fuming nitric acid on alkali, and finished with nitric acid. The barium sulfate is precipitated in the usual manner.

As there is always considerable silica formed from the glass it is necessary to evaporate twice with hydrochloric acid, thoroughly dehydrate, and remove the silica before precipitating the sulfate.

The results obtained by this method (Table II) show very good agreement.

TABLE II

Sulfur Insol. in Acetone, Sol. in Alc. KOH	Sulfur in Residue (Per cent Combined S)	Total Acetone-Insol. Sulfur Per cent
0.32	2.06	2.43
0.37	2.07	2.39
0.38	2.01	Av., 2.41
0.36	2.03	
0.32	Av., 2.04	
0.30		
0.32		
0.34		
0.34		
Av., 0.34		

The sum of the sulfur in the alcoholic potash and that left in the rubber is 2.38 per cent, which checks very well with the direct result on the total acetone-insoluble sulfur, *viz.*, 2.41 per cent.

Hence, the figure obtained for the combined sulfur after extraction with alcoholic potash is much more nearly correct than any obtained by methods which do not take into account the acetone-insoluble compounds of sulfur with resins and proteins. It is still possible that there is some sulfur combined with proteins and resins, insoluble in acetone and not attacked by alcoholic potash. For the present, therefore, the figure obtained by the method presented here must be considered as a maximum value for the coefficient of vulcanization.

APPLICATION OF METHODS

These methods were applied to a series of cures on a stock made up of 100 parts of pale crepe and 5 parts of sulfur. The results are given in Table III as parts of sulfur per 100 of rubber:

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[1] Hinrichsen and Memmler, "Der Kautschuck und seine Prüfung."

[2] *Kolloid-Z.*, 9, 300.

TABLE III

Cure Hrs.	True Free S	Sulfur in Alc.-KOH Extract	Coefficient of Vulcanization	Sulfur in Resin and S Compounds (Sol. in Acetone) (by Difference)
0.5	4.39	0.00	0.61	0.00
1.0	3.93	0.00	1.03	0.04
1.5	3.74	0.03	1.21	0.02
2.0	3.18	0.03	1.63	0.16
2.5	2.54	0.07	1.93	0.46
3.0	2.12	0.13	2.30	0.45
3.5	1.76	0.26	2.51	0.47
4.0	1.27	0.33	2.88	0.52
4.5	0.85	0.49	3.14	0.52
5.0	0.54	0.34	3.54	0.58

From these results it is evident that the theories of vulcanization proposed in the past, none of which took into account the formation of these compounds, are based on false figures and cannot be considered sufficiently accurate.

SUMMARY

Two new methods for rubber analysis are presented. The first gives the correct value for free or elementary sulfur in rubber goods, and the second a lower and more accurate value for the coefficient of vulcanization than can be obtained by any of the older methods. This work was all done on pure gum stock without any accelerator, and the methods developed are now being expanded to meet the conditions which obtain in compounded stocks.

DETERMINATION OF THE JELLYING POWER OF GELATINS AND GLUES BY THE POLARISCOPE[1]

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In the commercial production of gelatins or glues, the raw materials, such as hides, bones, sinews, etc., after certain preliminary treatment, are extracted with hot water in several successive operations or runs at successively higher temperatures. The first run or extraction, barring accidental changes or bacterial decomposition, yields gelatin of the highest jelly strength. The later runs diminish regularly in strength, probably because of the increasing time and temperature to which the raw material has been subjected. In a previous paper[2] it was pointed out that gelatins of the highest jelly strength approximated a definite and maximum value of mutarotation measured between 35° and 15° C. It was early conjectured and observed that the jellying power decreased in "weaker" gelatins parallel with the reduction of the mutarotation. The most probable explanation is that this is due to the decomposition of the gelatin molecules: *i. e.*, the percentage of actual gelatin which can exist in the two forms

$$\text{Sol form A} \rightleftarrows \text{Gel form B}$$

has been reduced. When the gelatin is practically all destroyed we have no mutarotation or jellying power and the product is the more or less indefinite β-gelatin.

The present polariscopic study of gelatins and glues correlated with certain physical tests including the "bubble standard" and mechanical devices, gives a good understanding of the relation of time, concentration, and temperature in the development of jelly strength. The results obtained have suggested a standard of comparison for measuring jellying power, based on the polariscope, which minimizes the usual multiplicity of arbitrary conditions of the various mechanical testers in use. This paper does not discuss the many existing types of mechanical testers in use, for no one of them has been found to be sufficiently widely used to make a useful comparison with the polariscopic method. Comparisons have been made only with certain physical tests and contrivances which have been developed in the laboratory.

In extending the study of gelatins of the highest purity to those of lower strength, it was thought important to study the following points in evolving the polariscopic method:

1—The constancy of the rotation per gram (or the specific rotation) at 35° C.

2—The changing and final nearly constant and increased rotation per gram when cooled from 35° to 15° or 10° C.

3—The gelation increment of mutarotation based on the "bubble standard" of jelly strength.

4—Comparison of the polariscopic method with mechanical methods.

The measurements reported in the previous paper were given in angular degrees. As most commercial laboratories are equipped with instruments using the Ventzke degree, the results are given in the latter unit. All readings are levorotatory.

ROTATION OF GELATINS AND GLUES AT 35° AND 15° C.

The samples were powdered and air-dried to minimize the great sensitiveness to changes in moisture, and preserved in stoppered bottles. After soaking weighed amounts in cold water in graduated flasks for about 30 min. they were dissolved on the steam bath between 50° and 60° C. and made up to the mark at 35°. Rotations at 35° C. were measured in 2 dm. tubes after immersion in a water bath for 15 min. It is preferable to have the temperature a degree or so above 35° when

TABLE I—ROTATION OF GELATINS AND GLUES AT 35° AND 15° C.

	Rotation at 35° C.		Rotation after 6 Hrs. at 15° C.				
SAMPLE No.	2 G. per 100 Cc.	5 G. per 100 Cc.	1 G. per 100 Cc.	2 G. per 100 Cc.	3 G. per 100 Cc.	5 G. per 100 Cc.	7 G. per 100 Cc.
436......	—13.40	—33.0	—9.0	—18.5	—28.6	—48.8	—68.8
Per gram......	6.70	6.60	9.0	9.25	9.53	9.76	9.83
166........	13.50	33.60	9.6	19.8	30.3	52.2	73.2
Per gram......	6.75	6.72	9.6	9.9	10.1	10.44	10.46
861........	13.40	33.5	10.0	20.6	31.5	53.4	75.0
Per gram......	6.70	6.70	10.0	10.3	10.5	10.68	10.71
912........	13.50	33.80	11.3	22.8	...	58.2	82.2
Per gram......	6.75	6.76	11.3	11.4	...	11.64	11.73
407........	13.65	34.0	11.3	23.0	35.1	59.2	82.8
Per gram......	6.82	6.80	11.3	11.5	11.7	11.84	11.83
171........	13.70	33.7	11.6	23.5	35.7	60.8	85.4
Per gram......	6.85	6.74	11.6	11.75	11.90	12.16	12.20
915........	13.90	34.1	11.55	24.0	36.5	62.4	87.0
Per gram......	6.95	6.82	11.55	12.0	12.17	12.48	12.44
858........	13.90	34.4	12.0	24.50	37.1	63.0	87.0
Per gram......	6.95	6.88	12.0	12.25	12.36	12.60	12.43
864........	13.9	34.5	12.1	24.60	37.1	62.8	87.6
Per gram......	6.95	6.90	12.1	12.30	12.36	12.56	12.51
671........	14.00	34.50	12.15	24.7	37.7	63.0	88.0
Per gram......	7.00	6.90	12.15	12.35	12.56	12.60	12.55
406........	13.50	33.5	12.5	25.5	38.8	65.2	91.8
Per gram......	6.75	6.70	12.5	12.75	12.93	13.04	13.10
859.	13.85	34.5	13.0	26.55	39.9	67.2	93.0
Per gram......	6.92	6.90	13 0	13.27	13.30	13.44	13.3
191	14.40	35.5	12.8	26.4	39.9	67.2	94.2
Per gram......	7.20	7.10	12.8	13.2	13.3	13.44	13.45
194........	14.40	35.70	12.9	26.7	40.7	68.0	...
Per gram......	7.20	7.14	12.9	13.35	13.56	13.60	...
405........	13.75	33.9	13.2	27.15	41.70	70.2	97.4
Per gram......	6.87	6.78	13.2	13.57	13.90	14.04	13.92

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[1] Published by permission of the Secretary of Agriculture.

[2] *J Am Chem. Soc.*, **41** (1919), 135

Table II—Mutarotation and Jellying Power

Number	Minimum Amounts that Produce Standard Jelly			Rot. ° V. of Standard Jellies		Gelation Increment of Rotation ° V.		Rot. ° V., 3 G. per 100 Cc. in Equilibrium			Mutarotation		Rot. per Gram at 15° C. for		Rot. per Gram at 10° C. for		Rot. 15° / Rot. 35°
	0° C.	10° C.	15° C.	10° C.	15° C.	10° C.	15° C.	35° C.	15° C.	10° C.	15° C.	10° C.	Minimum Amt. Conc.	3 G. Conc.	Minimum Amt. Conc.	3 G. Conc.	
								Bone Samples									
436	1.40	1.60	2.10	—18.0	—20.4	7.2	6.4	—19.8	—30.2	—33.5	10.4	13.7	9.7	10.1	11.2	11.2	1.53
166	1.15	1.25	1.60	14.8	16.6	6.4	5.9	20.2	32.4	35.4	12.2	15.2	10.4	10.8	11.8	11.8	1.60
861	1.10	1.20	1.45	14.3	15.7	6.3	5.9	20.1	33.4	35.4	13.3	15.3	10.8	11.1	11.9	11.8	1.66
192	1.00	1.10	1.40	13.8	15.3	6.2	5.6	20.6	34.1	37.4	13.5	16.7	10.9	11.4	12.5	12.5	1.66
195	0.92	1.05	1.40	13.3	15.0	5.9	5.2	21.0	33.8	38.0	12.8	17.0	10.7	11.3	12.6	12.6	1.68
912	0.81	0.86	0.96	11.2	11.3	5.4	4.9	20.3	36.6	39.8	16.3	19.5	11.8	12.2	13.0	13.3	1.80
407	0.70	0.78	0.88	10.1	10.8	4.8	4.8	20.4	37.6	40.4	17.2	20.0	12.3	12.5	13.0	13.5	1.84
171	0.70	0.78	0.89	10.6	10.7	5.4	4.7	20.4	36.8	40.7	16.4	20.3	12.0	12.2	13.6	13.6	1.80
858	0.70	0.75	0.77	10.5	10.0	5.2	4.8	20.5	40.0	42.0	19.5	21.0	13.0	13.3	14.0	14.0	1.95
864	0.68	0.73	0.80	10.0	10.1	5.0	4.6	20.7	39.0	41.8	18.3	21.1	12.6	13.0	13.7	13.9	1.88
671	0.67	0.73	0.78	9.9	10.1	4.8	4.7	21.0	40.2	42.0	19.2	21.0	13.0	13.4	13.6	14.0	1.91
742	0.70	0.75	0.80	10.3	10.2	5.1	4.8	20.7	40.0	42.2	19.3	21.5	12.8	13.3	13.7	14.1	1.94
406	0.62	0.67	0.72	9.6	9.4	4.8	4.6	20.1	40.0	42.5	19.9	22.4	13.0	13.3	14.3	14.2	1.99
915	..	0.65	0.72	9.2	9.6	4.8	4.7	20.5	41.6	43.0	21.1	22.5	13.3	13.8	14.1	14.3	2.03
191	0.61	0.65	0.70	9.5	9.5	4.9	4.5	21.3	42.0	43.8	20.7	22.5	13.6	14.0	14.6	14.6	1.99
859	0.57	0.62	0.68	9.0	9.3	4.7	4.6	20.7	43.2	44.2	22.5	23.5	13.8	14.4	14.5	14.7	2.09
194	..	0.62	0.67	9.2	9.5	4.8	4.7	21.4	43.9	45.7	22.5	24.3	14.2	14.6	14.8	15.2	2.06
169	0.57	0.62	0.67	9.0	9.4	4.7	4.7	21.0	42.8	45.0	21.8	24.0	14.0	14.3	14.8	15.0	2.04
168	0.53	0.56	0.58	8.5	8.5	4.6	4.5	20.8	44.4	46.4	23.6	25.6	14.7	14.8	15.2	15.4	2.14
405	0.53	0.56	0.58	8.4	8.5	4.6	4.6	20.3	44.9	46.5	24.6	26.2	14.7	15.0	15.3	15.5	2.21
393	0.51	0.54	0.55	8.5	8.4	4.7	4.6	21.3	46.2	47.0	24.9	25.7	15.3	15.3	15.7	15.6	2.14
								Hide and Sinew Samples									
1	0.50	0.52	0.55	8.2	8.4	4.6	4.6	20.9	45.0	46.0	24.1	25.1	15.3	15.0	15.7	15.3	2.15
2	0.62	0.65	0.69	9.6	9.5	5.1	4.7	20.7	41.2	42.6	20.5	21.9	13.7	13.7	14.7	14.2	1.99
3	0.76	0.82	0.88	10.9	10.7	5.1	4.6	21.1	38.0	41.0	16.9	19.9	12.2	12.7	13.3	13.7	1.80
5	0.57	0.60	0.64	9.0	9.3	4.7	4.7	21.5	44.2	45.0	22.7	23.5	14.6	14.7	15.0	15.0	2.06
6	0.63	0.65	0.69	9.5	9.5	5.0	4.7	20.7	42.4	43.6	21.7	22.9	13.8	14.1	14.6	14.5	2.05
7	0.52	0.53	0.57	8.0	8.4	4.4	4.6	20.5	43.6	45.0	23.1	24.5	14.7	14.7	15.1	15.0	2.12
8	0.74	0.77	0.80	10.6	10.1	5.4	4.7	20.3	39.0	40.8	18.7	20.5	12.9	13.0	13.7	13.6	1.92
9	0.83	0.87	0.95	11.3	11.3	5.4	4.9	20.4	36.3	38.8	15.9	18.4	11.9	12.1	13.0	12.9	1.78
10	0.77	0.80	0.87	11.0	11.1	5.4	5.0	21.0	38.4	40.6	17.4	19.6	12.9	12.8	13.7	13.5	1.83
11	0.86	0.90	1.09	11.4	11.8	5.2	4.9	20.6	36.2	39.0	15.6	18.4	11.8	12.1	12.7	13.0	1.75
12	1.15	1.20	1.35	14.4	15.0	6.2	5.4	21.3	33.2	36.9	11.9	15.6	11.1	11.1	12.0	12.3	1.56
A	1.10	1.25	1.60	14.4	16.2	6.0	5.5	20.2	31.8	34.6	11.6	14.4	10.1	10.6	11.5	11.5	1.57
B	1.75	2.30	3.50	21.8	29.3	6.8	6.4	19.6	25.6	28.6	6.0	9.0	8.6	8.5	9.5	9.5	1.31
C	2.30	3.00	5.30	25.8	40.3	6.8	6.8	19.0	22.9	26.0	3.9	7.0	7.6	7.6	8.6	8.6	1.20
Sin I	1.00	1.20	1.35	14.6	14.8	6.6	5.8	20.0	34.0	37.4	14.0	17.4	11.0	11.3	12.1	12.4	1.70
Sin C	1.40	1.80	2.60	17.7	22.3	6.1	5.6	19.3	27.2	29.6	7.9	10.3	8.5	9.0	9.8	9.9	1.41

working in a cold room so that the temperature of reading does not fall appreciably below the correct temperature.

When the solutions are cooled to 15° C. the changes in rotation parallel the increase in viscosity. As was shown in the previous paper, the reaction is essentially bimolecular, and we find that the rotations per gram of different concentrations change more rapidly in the higher concentrations, but as the change proceeds they approximate each other. The samples of Table I are supposed to be made from ossein stock. They represent only a small proportion of those examined, proving the conclusions applicable to gelatins and glues from hides, sinews, and other sources. Similar results have been obtained on many other samples and lead to the conclusion that the rotation per gram at 35° C. is nearly constant on all gelatins and glues.

The results show that at the end of 6 hrs. the rotation per gram of various concentrations at 15° C. approach each other, but the lower concentrations of 1 g. and 2 g. per 100 cc. are still somewhat slower.

MUTAROTATION AND JELLYING POWER

If the solutions are maintained at 15° (or 10°) over night (12 to 18 hrs.) the rotations finally reach constant values and represent the maximum change in rotation and jellying power at that temperature. These represent equilibrium rotations and corresponding equilibrium jellystrengths. The results given in Table II are particularly concerned with these equilibrium rotations and their corresponding jelly strengths rather than the development produced in a definite and comparatively limited period of time. In this table are assembled the results obtained on 40 samples of gelatins and glues arranged partly in the order of their jellying power and partly according to origin.

In the first three columns results are given the minimum amounts in grams per 100 cc. which will produce the standard jelly at 0°, 10°, and 15° C., respectively, when the maximum strength has been developed. The standard jelly is such that a bubble of air 4 to 5 mm. in diameter admitted to the polariscope tube moves vertically with a scarcely perceptible motion of 4 cm. per second. It is sufficient to maintain the solution in a constant temperature bath over night (16 hrs.). No appreciable change in viscosity or optical rotation takes place on extending the time indefinitely.

In the next two columns are given the rotations in ° V. of the standard jellies obtained with the corresponding minimum amounts of the two preceding columns.

In the sixth and seventh columns are given the increments in rotations obtained by subtracting the rotations of the respective minimum amounts at 35°, calculated from the rotations of the 3 g. concentrations at the same temperature given in the eighth column, from the rotations of the standard jellies at their respective temperatures.

In Columns 9 and 10 are given the mutarotations between 35° and 15° C., and between 35° and 10° C., obtained by subtraction of the respective rotations.

In the next two columns are given the increments in rotation between 35° and 15° C., and between 35° and 10° C., obtained by subtraction of the respective rotations.

In the next four columns are given the calculated rotations per gram based on the minimum amount concentration and the 3 g. concentrations at 10° and 15° C.

In the last column is given the ratio of rotation at 15° to the rotation at 35° C.

The bone samples are known to be so on representation and by odor. Those given as hide or sinew samples were obtained directly from the manufacturers by special arrangement. Only the last two samples are sinew samples and are designated Sin I and Sin C.

Selecting Sample 405, for example, 0.53 g. per 100 cc. just produces the standard jelly at 0°; 0.56 g. per 100 cc. is necessary at 10°; and 0.58 g. at 15° C. In these concentrations the standard jelly persists indefinitely. The rotation of 0.56 g. in the condition of the standard jelly is —8.4° V. at 10°. The rotation of 0.58 g. at 15° C. is 8.5° V. 0.56 g. of Sample 405 at 35° rotates —3.7° V. (calculated from 3 g. per 100 cc. at 35°), hence the increment of rotation is 8.4 — 3.7 or 4.7° V. (corresponding to 0.81 circular degrees in 1 dm. tube). Similarly the increment at 15° C. is 4.6° V. Three grams of Sample 405 per 100 cc. rotate —20.3 at 35° C., —44.9 at 15°, and —46.5 at 10° C., which gives us 24.6° V. and 26.2° V. as increments at 15° and 10° C., respectively. The rotation per gram at 15° C. is —15.0 (14.96); calculated from 3 g. concentration, —15.0 (14.96); and that calculated from 0.58 g. at 15° is —14.7. Similarly the rotation per gram at 10° C. calculated from 0.55 g. concentration is —15.3 as compared with 3 g. concentration of —15.5.

The samples showing the greatest mutarotation in the 3 g. per 100 cc. concentration require the smallest amounts to produce the standard jelly. As the mutarotation decreases, the amounts required to produce the standard jelly increase. Some of the "strongest" gelatins show about 8 per cent increase in strength passing from 15° to 0° C., and about 4 per cent from 15° to 10°.

It will be noted that the rotations at 35° C. of 3 g. per 100 cc. of air-dry samples vary between —21.5 and —19.6° V., decreasing ratherirregularly from the "strong" gelatins to the "weak" ones. Probably this irregularity is due to variations in ash and moisture content. It is to be noted that the gelatin increment of rotation is approximately 4.6 to 4.7 at 15° or 10° C. in the strongest gelatins. For these, their jellying power between 15° and 10° (and probably at 0°) varies inversely as the extent of their mutarotation. We may make the highly probable assumption that in more concentrated solutions the same ratios of strength will be preserved. In the weaker gelatins the increment of gelation increases gradually up to about 7.2 in the weakest gelatin. It is obvious that the inverse relation does not hold in these gelatins if compared with much stronger gelatins for the apparent mutarotation is greater than the jelly strength developed would indicate.

In the weaker samples, a large proportion of non-gelatin substance might either increase or decrease the true mutarotation. To study this point, comparison was made between Hide I and Hide C gelatins, cooling them rapidly from 35° to 15° C. in the minimum amount quantities. The following readings were obtained:

	Rotation at 35° C.	1 Min. 15° C.	2 Min. 15° C.	3 Min. 15° C.	Equilibrium 15° C.
Hide I.............	—3.8	—3.8	—3.9	—3.9	—8.4
Hide C.............	—33.5	—34.8	—34.8	—34.9	—40.3

These results show that the great change in rotation of Hide C, at the end of one minute, which does not represent true mutarotation, accounts for a change of about 1.3 points. This subtracted from the observed increment of 6.8 as given in the table gives us 5.5 points of true mutarotation. To test this point further, a sample of gelatin was heated in solution for several days until a 50 per cent solution would not produce a gel. This was examined polariscopically and showed little or no mutarotation, but a great increase in levorotation, when cooled between 35° and 15°. It is quite evident that our apparent gelatin increment of mutarotation is increased by the change in the β-gelatin present in increasing amounts as the jelly strength diminishes.

POLARISCOPIC METHOD AND APPLICATIONS

The writer has selected 15° and 10° C. as standard temperatures for jelly strength comparisons rather than higher temperatures which represent more active equilibrium between the sol and gel forms. This is apparent from the results and figures of melting points on gelatins of high jellying power in the previous paper and is even more pronounced in weak gelatins or glues where we find considerable difference in the strength developed even between 10° and 15° C. Further, the chest or "cool place" in which food gelatin may be set and preserved is not likely to be higher than 15°.

In grading gelatins or glues, polarize 3 g. per 100 cc. at 35° to 36° C. in a 2-dm. tube; cool a portion of the solution rapidly to 15° (or 10°) and transfer before the sample has jellied to a cold 1-dm. tube. This procedure avoids contractions in the jelly which may produce poor readings. If the samples need clarification digest the solution with 5 cc. of light powdered magnesium carbonate at 30° to 40° C. for one hour or longer, and filter until clear, avoiding appreciable evaporation. Occasionally it has been found advantageous to add 0.10 g. of ammonium citrate to the filtrate to avoid the formation of insoluble calcium compounds, but this does not appear to be necessary if the magnesium carbonate has been used in sufficient quantity and the digestion has not been too short. The procedure for clarification outlined has not been found to change the polariscopic results when applied to clear samples.

In place of a constant temperature bath the tubes can be placed in a large vessel of water in a portion of the ice chest where the temperature ranges between 13° and 16° and left over night. The next day the temperature can be controlled for 4 to 7 hrs. at 15 ± 0.4°. If a constant temperature bath is used the tubes may be read at once in the morning.

Considering a sample which polarizes —20.5° at 35° C. and —40.0° at 15° C. in a concentration of 3 g. per 100 cc., it is suggested that the strength be expressed as 19.5 points at 15° C., the increment in rotation in Ventzke degrees. Referring to Table II we see that a 25-point gelatin at 15° represents the maximum strength obtained. In factory control the jelly strength determinations can be made by the polariscope in the progress of the extractions, evaporation, or drying. The solutions are diluted to approximately 3 g. per 100 cc., controlled by rotations at 35° C. The jelly strength at 15° is determined as usual and calculations made by simple proportion to reduce rotations to an average basis of —20.5° V. at 35° C. An actual test in factory control gave the strength of a first extraction as 17 points at 15° C.; after evaporation it was 10 points. The evaporated extract was mixed with some unevaporated material bringing the strength to 11.5 points; after drying it tested 11.6 points. These figures obviously represent poor extraction, and considerable loss of strength in the evaporator, but show no loss from bacterial action in drying.

Jelly strength tests made on samples direct and after incubation for 24 hrs. at 37° C. show little or no loss in strength of nearly sterile gelatins, while those in active state of decomposition show considerable loss with the development of bad odors. The following results illustrate this:

No.	35° C. 3 G. per 100 Cc	Rot. at 15° C. before Incubation	Rot. at 15° C. after Evaporation	Odor after Evaporation
1	—20.3	—33.4	—33.8	Sweet
2	—20.5	—39.7	—36.8	Bad
3	—20.3	—35.6	—31.6	Bad

The solutions were filtered through magnesium carbonate to clarify. The increase in rotation in No. 1 was probably due to evaporation and experimental error. The loss of jelly strength in Nos. 2 and 3 was quite pronounced, with corresponding production of disagreeable odors.

A progressive increase in levorotation (or mutarotation) obtained from a solution cooled quickly below 35° C., accompanied by the production of a jelly after a change of approximately 4.7° V., is very positive proof of the presence of gelatin in any solution concentrated enough to jelly.

JELLY STRENGTH MEASUREMENTS BY A MECHANICAL TESTER

Several different mechanical testers have been developed in the laboratory but only one, which recommends itself as accurate and requiring a small amount of sample, is here described. The bubble test is accurate to about 3 per cent on high strength gelatins comparing quantities which just produce the standard jelly. We have seen that the minimum amounts necessary for jelly production change in a definite way following the mutarotation. It was thought desirable to make certain that similar relations existed in much higher concentrations.

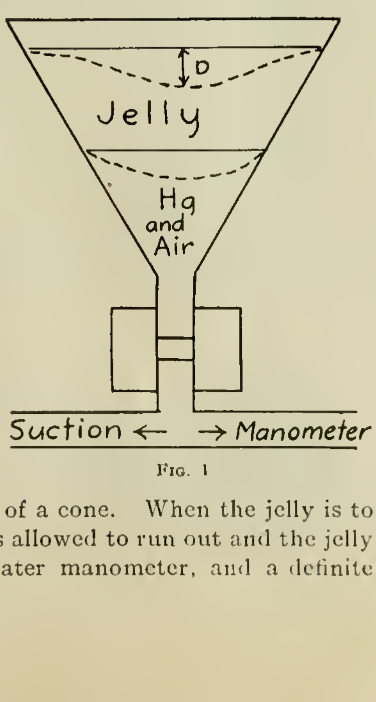

Fig. 1

Fig. 1 represents an 80 mm. glass funnel with short stem accurately formed to a 60° angle. Mercury weighing 120 g. is poured into the funnel closed at the end. The diameter at the surface of the mercury is 3 cm. Fifty cc. of the gelatin solution are poured over the mercury and allowed to solidify in a horizontal position (determined by spirit level) in a constant temperature bath at 10° C. We have now formed a definite sized reproducible jelly in the shape of the frustrum of a cone. When the jelly is to be tested the mercury is allowed to run out and the jelly is connected with a water manometer, and a definite reduction of pressure is produced (6 dm. of water), which causes a depression in the jelly which can be measured by a micrometer depth gage reading to thousandths of an inch. Some results are given in Table III.

Table III—Mechanical Tests at 10° C.

Sample No.	Displacement in Inches by Partial Vacuum 6 Dm. Water	Rotation Increment 10° C.
393	0.137	25.7
168	0.135	25.6
407	0.269	20.0
859	0.218	23.5
1	0.136	25.1
7	0.151	24.5
169	0.220	24.0

SOME PHYSICAL CONSTANTS OF PURE ANILINE[1]

By C. L. Knowles

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The importance of aniline to the dye industry has long been recognized, but no practical method of analysis has been available for general use in judging its quality. An attempt has therefore been made to find a method of analysis or test which would not only be accurate, but of such a nature that it could be applied quickly and easily in the control of the manufacture of this product.

A survey of chemical methods of analysis disclosed the fact that, due to the rather large experimental errors, most of them fail when the purity of the aniline exceeds 99.5 per cent. Attention was therefore turned to the possibilities of the application of the physical constants for accurately judging the purity. It would naturally be expected that the physical constants of such a common intermediate would long since have been established beyond any reasonable question. As a matter of fact, a great number of investigators have made a study of aniline but, instead of establishing these points, widely diverging results have been published.

On consulting the literature, no less than 16 different values for the freezing point of aniline were found. These varied between —8° and —5.96° C., while values for the boiling point ranged from 182.5° to 184.8° C. Of the numerous results given, the only ones considered were those in which the method of purification and methods of recording temperatures were fully described. The following have been chosen as most reliable, and are those generally accepted: Ampola's freezing point of —5.96°, Timmermans' of —6.20°, and that of Jones and Sanderson of —6.00° C. The latter has been published since the completion of this work, along with a formula for determining the purity of aniline from its freezing point. Timmermans, Callender, and Beckman apparently give the most accurate boiling points, their results being 184.40°, 184.10°, and 184.30° C.

Since no conclusions could be drawn from these results, it was necessary to prepare a sample of pure aniline, and to determine accurately its physical constants. In the course of this work it was soon discovered why so many different values had appeared for the physical constants of aniline, since to purify aniline and maintain it in a pure state was found to be a matter of considerable difficulty.

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[1] Presented at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

PREPARATION OF THE SAMPLE

Two liters of colorless aniline were distilled *in vacuo* four times, rejecting the first and last portions in each case. The product thus obtained was allowed to drop slowly into a saturated solution of recrystallized oxalic acid. The aniline oxalate was filtered off, washed several times with water, and three times recrystallized from 95 per cent ethyl alcohol. The salt was washed with pure ethyl ether after each crystallization. In order to regenerate the aniline, a saturated solution of recrystallized sodium carbonate was added, the aniline distilled off, and distilled *in vacuo* three more times. When possible, determinations were made immediately on the sample. When this could not be done, the material was kept in a darkened vacuum desiccator.

DETERMINATION OF PHYSICAL CONSTANTS

BOILING POINT—For the boiling-point determination a standard Beckmann boiling-point apparatus was used, readings being taken by means of a platinum resistance thermometer. This apparatus had been recently standardized by the U. S. Bureau of Standards for three points: for ice, the boiling point of water, and the boiling point of sulfur. The manufacturers guaranteed an accuracy of 0.01°. Before and after each determination the thermometer was further checked against the ice point and freezing point of benzene. It is of interest to note that we were able to check very well the freezing point of benzene, obtaining 5.486° C., as compared with 5.493° C. ± 0.007 as obtained by Richards.[1]

Following all precautions mentioned later, we obtained consistently a boiling point of pure aniline of 184.32° to 184.39° C. at 760 mm. pressure.

FREEZING POINT—Immediately after vacuum distillation, the pure sample (10 to 15 cc.) was transferred to a test tube surrounded by a larger glass tube, and supported at the top by a thin ring of asbestos. The platinum resistance thermometer and a stirrer were inserted, and the whole immersed in a brine mixture at —10° to —12° C. The sample was stirred at a uniform rate and the freezing point determined. It was found to be —6.24° C., consistent checks being obtained.

SPECIFIC GRAVITY—Specific gravity determinations were made on the freshly distilled sample in a pycnometer at 15° C., and compared with water at the same temperature, giving a value of 1.0268 at 15°/15° C.

REFRACTIVE INDEX—The index of refraction was determined by means of an Abbé refractometer, manufactured and calibrated by the Zeiss Instrument Co. The best samples of aniline had an index of refraction of 1.5850 at 20° C.

PRECAUTIONS OBSERVED

Numerous articles have been published in reference to the effect of air and light on aniline. While this phase of the subject is of great interest, it is manifestly beyond the scope of this paper. It has been noted that the purer the sample of aniline the more stable it is toward air and light. Our purest samples have darkened but slightly when kept in diffused light for months.

EFFECT OF MOISTURE—One property of aniline which caused considerable trouble in our work, and which apparently has received but very little attention in the past, is its extreme hygroscopicity. It is believed that this alone accounts to a large extent for the conflicting results found in the literature. If aniline in the pure state be exposed to the air for but one hour, the freezing point and boiling point are materially affected; consequently extreme care must be taken in determining constants of the pure material. If undue time is required for these determinations, no accurate figures can be obtained. For this reason all samples were freshly distilled *in vacuo*, and determinations made as rapidly as possible. In order to check these results, attempts were made to determine freezing points *in vacuo*, but due to the mechanical difficulties encountered, no results of value were obtained. Results of both freezing-point and boiling-point determinations made in an atmosphere of dry inert gas, such as nitrogen or carbon dioxide, were identical with those of determinations made rapidly in the presence of air.

In order to clearly demonstrate the effect of moisture on the purity of aniline, freezing points were made hourly on a sample exposed to the air. The initial freezing point was —6.35° C.; after 1 hr. it had fallen to —6.60° C.; after 16 hrs. it was —7.30° C.; and after 46 hrs. a freezing point of —8.20° C. was obtained. Assuming the formula for water at 0° C. to be $(H_2O)_4$,[1] this represents 2.4 per cent water absorbed; based on the molecular weight of water as 18, the amount of water present becomes 0.6 per cent.

The effect of entrained air and diminished pressure on freezing points has been carefully studied by Richards.[2] He concludes that the error due to vacuum is practically negligible, as is also that due to dissolved air in the case of benzene.

DISCUSSION OF RESULTS

The following have been chosen as the most reliable of previous freezing-point determinations:

	YEAR	Freezing Point ° C.
Ampola and Rimatori	1897	—5.96[1]
Timmermans	1911	—6.20[2]
Jones and Sanderson	1920	—6.00[3]

[1] *Gazz. chim. ital.*, [1] **27**, 35.
[2] *Bull. soc. chim. belg.*, **25** (1911), 300.
[3] *J. Soc. Chem. Ind.*, **39** (1920), 87.

For boiling points the following appear fairly reliable:

	YEAR	Boiling Point ° C.
Callender	1899	184.10[1]
Timmermans	1911	184.40[2]
Beckmann	1914	184.30[3]

[1] *Phil. Mag.*, [5] **48** (1899), 519.
[2] *Bull. soc chim. belg.*, **25** (1911), 300.
[3] *Z. physik. Chem.*, **89** (1914), 112.

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[1] *J. Am. Chem. Soc.*, **41** (1919), 2019.

[1] *Z. physik. Chem.*, **12** (1893), 433.
[2] *Loc. cit.*

Ampola and Rimatori purified their samples of aniline by repeated freezing out of the material. A repetition of their work gave in all cases a freezing point considerably lower than —6.24° C. The only explanation we have to offer is that their Beckmann thermometer might have been in error. The use of the Beckmann thermometer is considered bad practice for accurate work of this kind, since the standardization is difficult and the stem correction excessive.

Timmermans' determinations were made on carefully purified aniline, measurements being made by means of a platinum resistance thermometer. We have been able to check these results fairly well.

Jones and Sanderson purified their samples by crystallization, followed by drying and distillation over caustic soda. Temperature measurements were made by means of a mercury thermometer and the freezing point of pure material calculated. We have carefully repeated this work, but failed to get a freezing point as high as that given in their report. We are at the present time taking this point up with Professor Jones, hoping that in this way, we may be able to arrive at the true results. As an alternative to the method of purifying aniline by formation of the oxalate, it has been found that repeated vacuum distillation gives material of the same freezing point. Samples prepared from recrystallized acetanilide were not of a high degree of purity.

VALUE OF FREEZING POINT DETERMINATION

In comparing the chemical analyses and physical constants of a large number of samples of aniline, it has been noted that the freezing point determination is by far the best criterion of its purity. This method is being used in this laboratory to determine the purity of commercial samples of aniline.

By chemical analysis it has been shown that the impurities most frequently found in aniline are nitrobenzene, toluidine, and water, these being present in most samples tested in the ratio 2 : 4 : 10.

In order to have available a short expression for converting the freezing point of a sample directly to purity, use has been made of the plan described by Jones. However, it will be noted that the figures used are different, due to the difference in freezing points of the pure samples of aniline upon which the expressions have been based. Jones[1] determined the impurities present and assumed an average molecular weight for them. Substituting this value in the cryoscopic molecular weight formula he obtained a simple expression in which the freezing point may be substituted directly, giving the per cent aniline in the sample. Assuming 82.67 to be the average molecular weight of the impurities, the following formula may be used:

$$X = 108.79 + 1.41t,$$

when X = per cent aniline present in the sample, and t = the observed freezing point in ° C.

In developing this formula it was necessary to accept the cryoscopic constant of Ampola (5870). Should this be slightly in error, the discrepancy in the result will be practically negligible. This is also the case when the relation of impurities is altered.

SUMMARY

1—It is believed that the following are the true physical constants of aniline:

Freezing point	—6.24° C.
Boiling point	184.32°, 184.39° C. at 760 mm.
Specific gravity (15°/15° C.)	1.0268
Refractive index (20° C.)	1.5850

2—The indications are that the freezing point is the best criterion of the purity of aniline.

3—In order to calculate the purity of a sample of aniline from its freezing point, use should be made of the formula:

$$X = 108.79 + 1.41t.$$

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[1] *J. Soc. Chem. Ind.*, **39** (1920), 8*t*.

THE DETECTION AND ESTIMATION OF YELLOW AB AND YELLOW OB IN MIXTURES[1]

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The dyes benzeneazo-β-naphthylamine (Yellow AB) and *o*-tolueneazo-β-naphthylamine (Yellow OB) are at present the only oil-soluble coal-tar colors that may be used in food products without objection by the U. S. Department of Agriculture, and for this reason properties that can be applied to the chemical examination of mixtures containing them are of some special interest. Cornelison[2] and Lubs[3] have described methods for separating them from colored fats and oils and identifying them.

PREVIOUS INVESTIGATIONS

Several years ago the writer carried out some experiments with these dyes in connection with the study of general methods[4] of color analysis. Attempts to separate them from colored salad oils by diluting the products with 2 to 4 volumes of gasoline and shaking out with a mixture of phosphoric and sulfuric acids gave unsatisfactory results, especially in the case of Yellow OB, for although the dye was removed quite readily from the oil-gasoline solution a large proportion of it, usually 50 per cent or more, was destroyed in the process. The behavior of the dyes in other acid mixtures, as for example, ether and hydrochloric acid, was also somewhat peculiar. The coloring matter was apparently very slowly extracted from ether by shaking with 5 *N* hydrochloric acid, forming a red solution in the acid that gradually faded, so that on standing over night both layers became colorless. As compounds of this class are known to exist in several different forms, it was supposed that the form more readily extracted was not present in any considerable amount in the organic solvent solutions and was produced rather slowly under the influence of the dilute acids used. At the time these tests were made Yellow AB and Yellow OB apparently were not being used in food products and were said to be off the market, so no further attention was given to the matter. Lubs[1] found later that practically no Yellow OB was extracted from 0.002 per cent solutions in gasoline by shaking with 4 to 6 *N* hydrochloric acid. H. A. Lubs and A. B. Clark[2] also measured spectrophotometrically the rate of decomposition of Yellow OB in a mixture made by diluting 2 cc. of 0.4 per cent alcoholic solution of the dye to 100 cc. with a solvent prepared from 90 cc. glacial acetic acid, 10 cc. water and 10 cc. concentrated sulfuric acid. The loss observed in the first half hour was about 2 per cent, in the first 5 hrs. about 15 per cent, and in the first 75 hrs. about 67 per cent.

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[1] Published by permission of the Secretary of Agriculture.

[2] *J. Am. Chem. Soc.*, **30** (1908), 1478.

[3] This Journal, **10** (1918), 436.

[4] U. S. Dept. of Agriculture, *Bulletin* **448**.

The dyes are quite reactive substances, and it seemed not improbable that the results obtained in the first experiments had been influenced by impurities in the reagents, the presence of oxides of nitrogen in the phosphoric acid, and aldehydes in the ether being suspected in particular.[3] The test with 5 *N* acid and ether has been repeated with reagents now in stock, and the slow passage of the coloring matter into the acid layer and its subsequent disappearance noted exactly as before (the acid used was made by diluting ordinary C. P. acid, while the ether was of U. S. P. grade). In view of the results obtained with gasoline and described below, it was not thought necessary to make further study of the ether mixtures. The solutions commonly used for tests of this kind are very dilute so that quite minute quantities of reactive impurities in the reagents are sufficient to alter a large proportion of the coloring matter.

EXPERIMENTAL PART

The experiments discussed in the present paper were made mainly to form a basis for quantitative methods. It was found that light ("low b. p.") gasoline and dilute sulfuric acid in concentrations ranging from 3 to 25 *N* gave a set of solvents fairly satisfactory for work with these dyes and which, although somewhat unpleasant to use, were not worse in this respect than any others that could be selected. In order to remove any traces of nitrous acid or free halogens from the acid, the mixtures were treated with hydrazine sulfate in the proportion of 1 g. per liter, most of the salt crystallizing out again on standing. The specific gravity of the mixtures corresponded almost exactly with those of pure dilute acid of the same concentration.

When solutions of Yellow AB in commercial low-boiling gasoline were shaken with dilute sulfuric acid of such concentration as to extract a part of the dye, some of the latter was changed into an orange substance which was relatively much more soluble in the acid layer than the dye itself. It could be separated by diluting the acid solution with half its volume of water, removing unchanged dye with gasoline, neutralizing, and extracting with ether. The gasoline used for the tests was purified in two liter lots by treating with 0.5 to 1.0 g. Yellow AB, then shaking out with four or five 200 cc. portions of concentrated sulfuric acid, the liquids being allowed to stand together for some time. A glass-stoppered bottle was used for the mixing, the wash acid being removed or blown out with a wash-bottle fitting. With this purified gasoline very little or none of the orange product just mentioned was formed. The specific gravity of this gasoline $\left(\frac{20^\circ\text{ C.}}{20^\circ\text{ C.}}\right)$ was 0.6460, and when heated on the water bath, about 70 per cent distilled between 38° and 55° C.

RESULTS WITH VARIOUS DYES—When gasoline solutions of Yellow AB containing about 0.005 g. dye per 100 cc. are shaken with dilute sulfuric acid, little or none of the coloring matter passes into the acid solvent unless its acidity is above 7 *N* (3.5 moles per liter). With acid 16 *N* or stronger (to 25 *N*) practically all dye is removed from the gasoline. Yellow OB shows similar behavior, but is relatively somewhat more soluble in the gasoline so that the acid concentrations corresponding to the limits just given are about 10 and 18 *N*. The other common oil-soluble dyes are quite different in relative solubility, aminoazobenzene (Aniline Yellow), aminoazo-*o*-toluene and dimethylaminoazobenzene (Butter Yellow) passing in chief proportion into the acid when this is 7 *N* or stronger, while benzeneazo-β-naphthol (Sudan I), *m*-xyleneazo-β-naphthol (Sudan II), benzeneazo-benzeneazo-β-naphthol (Sudan III), and α-naphthaleneazo-β-naphthol (Carminaph Garnet) remain in chief quantity in the gasoline when the acid concentration is not greater than 18 *N*. The variation in relative solubility with acid concentration is not so marked with benzeneazophenol, benzeneazoresorcinol (Sudan G) and α-naphthaleneazo-α-naphthol (Sudan Brown), but the first two in gasoline and 7 *N* acid mixtures appear to go in larger proportion into the acid. No tests were made with good preparations of these three dyes and the commercial products available were very impure. However, these coloring matters, because of their reactive phenolic character, will ordinarily be separated most conveniently from the β-naphthol and amino derivatives first named by the use of alkaline solvents. Benzeneazo-α-naphthylamine and aminoazo-α-naphthalene are removed from gasoline by 7 *N* acid, but a large proportion of the dye is precipitated, as it appears that the salts formed are not soluble in acid of this concentration. *p*-Tolueneazo-β-naphthylamine behaves similarly to Yellow OB, as might be expected, and *m*-xyleneazo-β-naphthylamine differs from Yellow OB about as that dye differs from Yellow AB. All of the dyes are removed almost completely from gasoline solution by shaking with 24 to 25 *N* sulfuric acid.

Benzeneazo-α-naphthol, bixin, and curcumin are practically insoluble in gasoline, so that they could not be tested directly.

TESTS FOR YELLOW AB AND YELLOW OB—The difference in solubility of Yellow AB and Yellow OB from most of the other dyes has occasionally been applied as a convenient test for the latter in mixtures. A gasoline solution is prepared containing about 0.005 g. dye per 100 cc., and 30 cc. are shaken out first with 1 or 2 cc. portions of 7 *N* sulfuric acid, then with two portions of 18 *N* acid, and finally, if the gasoline still contains color, with 24 *N* acid.[1] A trace of Yellow

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[1] *Loc. cit.*

[2] THIS JOURNAL, **10** (1918), 438.

[3] Krauch, "Die Prüfung der Chemischen Reagentien," 3rd Ed., pp. 8 and 310.

[1] The solvents must be vigorously shaken together for at least half a minute. If the 7 *N* acid extract is reddish it may be shaken with an equal volume of gasoline to remove Yellow AB.

AB may come out with the 7 *N* acid, but the 18 *N* acid will contain practically all of the coloring matter when only Yellow AB and Yellow OB are present. Carrotin and some of the coloring matters found in annatto seem to remain chiefly in the gasoline even after the shaking with 24 *N* acid, though bixin is taken out by acid of this concentration. The ordinary liquid mixtures sold as food colors consist of 2 to 3 per cent solutions of the dyes in oil and have been tested directly after diluting with from 500 to 1000 parts by volume of gasoline. If the amount or concentration of dye in a mixture under examination is quite unknown, it can be fixed closely enough by matching against a standard made by dissolving 0.005 g. of Yellow AB in 100 cc. gasoline. The acid used for qualitative tests has not usually been treated with hydrazine sulfate, or carefully standardized, being made by diluting measured amounts of the concentrated C. P. acid, which is about 35 *N*, cooling, and bringing to definite volume. Unpurified low-boiling gasoline gave fairly satisfactory results for such tests.

QUANTITATIVE SEPARATION—The differences in relative solubility of the different dyes are not great enough in many cases to permit a quantitative separation being made by a single shaking-out operation. Experiments were made with Yellow AB, Yellow OB, Butter Yellow and Sudan I to learn their behavior when subjected to a systematic fractionation procedure, the conditions being fixed with especial regard to the separation of Yellow AB and Yellow OB from each other and from other dyes.

A solution of 0.00400 g. dye in 40 cc. of gasoline was washed or shaken out with four 20 cc. portions of the dilute acid. Two additional separatory funnels containing 40 cc. portions of gasoline were provided and each acid washing portion, after being drawn out of the first separatory funnel, was shaken out successively in the second and third funnels. A fifth additional 20 cc. portion of acid was shaken in the second and third funnels and finally a sixth portion in the third. The gasoline extracts were combined, washed by shaking with water, then with a dilute solution of sodium acetate and acetic acid, and finally again with water. The gasoline was driven off on the steam bath, care being taken to avoid volatilization of the dye, and the residue dissolved in 93 per cent alcohol. The alcoholic solution was diluted to exactly 100 cc. (or to 25 cc. when it was not strongly colored), the light absorption constant at 0.436μ determined and the amount of dye calculated, using the figures for extinction coefficients given in the latter part of this paper. The acid portions or washings were combined, diluted with an equal volume of water, the dye extracted by shaking with two portions of gasoline, and the gasoline solution thus obtained treated in the same manner as the one first described.

The dilute acids were saturated with hydrazine sulfate as stated and are designated as 10, 13, and 16 *N*, the exact strengths as determined by titration being 10.17, 13.01, and 15.95. The specific gravities $\left(\frac{20^\circ \text{ C.}}{20^\circ \text{ C.}}\right)$ by pycnometer were, respectively, 1.2915, 1.3637, and 1.4370.

Tests were made by the procedure first described, using 13 *N* acid and Yellow AB. Four and eight-tenths per cent of the dye was recovered from the gasoline, 92.2 per cent from the acid. With Yellow OB under similar conditions 83.5 per cent was recovered from the gasoline, 10.1 per cent from the acid. In experiments made with 16 *N* acid the procedure was modified by omitting the use of a third funnel. Four portions of acid were passed through the first and second funnels and a fifth portion through the second. The figures obtained under these conditions with Sudan I corresponded to a recovery of 0.4 per cent from the acid, and 100 per cent from the gasoline. The parallel test with Yellow OB showed that but 1.0 per cent of the dye remained in the gasoline. The amount in the acid was not estimated carefully, but a colorimetric comparison indicated 90 per cent or more of the amount originally taken.

When 10 *N* acid was used the original procedure was modified by omitting the last three washings or acid portions. An experiment with Butter Yellow showed that under such conditions but 0.5 per cent remained in the gasoline. The dye in the acid was estimated roughly by colorimetric comparison and appeared to correspond to practically the amount originally taken. A similar test with Yellow AB showed the acid washings to contain but 0.9 per cent of the dye taken. (When the funnels were washed according to the original procedure 4.0 per cent of the dye was found in the acid.)

The experiments show that Yellow AB and Yellow OB can be separated by means of dilute sulfuric acid and gasoline from Butter Yellow and Sudan I and presumably from most other common oil-soluble dyes to a degree meeting the requirements of ordinary quantitative work. The optical data for the total mixture are readily obtained, so that the amount of Yellow AB or Yellow OB (or the sum of the two when both are present) may be determined by difference. In fractionating a mixture of two dyes in which one is present in relatively small proportion, the conditions can be shifted rationally to give more accurate results, for example, by using a larger number of portions of the solvent in which the predominating dye is more soluble. Although the distribution ratios vary more or less with concentration, and usually to a degree that make such analytical processes unmanageable with colorless substances, the course of the separation is apparent to the eye in the case of dyes. The fractionation methods for this reason possess a reliability and flexibility with dyes that they quite lack with other compounds.

When making separations with dilute sulfuric acid, special care has always been taken to see that the stoppers and stopcocks of the funnels were seated firmly before making the shakings, and the funnels have been held at the top neck, the latter being covered with a filter paper cap to protect the hand. Butter Yellow and the other dyes more readily soluble in aqueous liquids can, however, be fractionated as satisfactorily with less corrosive solvents. A mixture of Sudan I and Butter Yellow (at one time in common use) is separated in this laboratory with 4 *N* hydrochloric acid and ether (using two portions of each of the solvents).

A satisfactory quantitative separation of mixtures of Yellow AB with Yellow OB cannot be made with 13 *N* sulfuric acid unless a more elaborate procedure is followed than that described. The method considered best for such mixtures consists in carrying through a fractionation (usually with two or three funnels) choosing such conditions that practically all of one of the dyes will be removed from either the gasoline or the acid. The amount of the pure color remaining is determined and a correction made by comparing with the results obtained with known solutions or mixtures carried through in the same way. The quantitative separation of these dyes from dilute oil solutions, such as colored oleomargarine or salad oil, has not been carefully studied, but it is believed that a simple adaptation of the qualitative method of diluting the oil with a few volumes of gasoline and extracting with a strongly acid solvent gives very unreliable results.

ESTIMATION OF DYES—The dyes have been estimated in all cases by means of the spectrophotometer[1] after the removal of interfering substances. A König-Martens instrument was used but, instead of the absorption cell with glass cube or Schulz body employed for work described in a preceding paper,[2] a double cell was used, one compartment being filled with the solution under examination, the other with the pure solvent. This cell consisted of three plane parallel glass plates held together by two U-shaped pieces of steel serving as clamps. The middle plate was exactly 1 cm. in thickness and contained two circular holes at the middle, forming the cavities. These cavities were 2 cm. in diameter and 0.2 cm. apart and were filled by means of small vents 0.5 cm. in diameter drilled through one of the edges of the plate. This cell gave no trouble because of leakage, was easily cleaned, and furnished results requiring no correction for absorption, reflection, and refraction of the glass and solvent. A similar cell was also tried in which the middle plate was of brass and channeled near the edges so that a stream of water at constant temperature could be passed through it. Such a plate would also give less error from scattering light, but the one tried was not accurately finished, and could not be made tight. The glass cell was held in a heavy brass carrier and adjusted to insure the full and symmetrical illumination of the slits of the spectrophotometer. A quartz mercury lamp was used as a light source, the instrument being set to show the blue line 0.436μ. The specific absorption for light of this wave length is very high with dyes examined, though the peaks of their absorption curves are somewhat further toward the green in most cases.[3]

Solutions of purified preparations of the dyes in alcohol of specific gravity $\left(\frac{25^\circ \text{ C.}}{4^\circ \text{ C.}}\right)$ 0.8055 (93.0 per cent by weight), containing 0.002 g. per 100 cc., gave values for the extinction coefficients as shown in the table.

DYE	EXTINCTION COEFFICIENT
Butter Yellow	1.86
Yellow AB	1.12
Yellow OB	1.09
Sudan I	0.86

The figures calculated from measurements made with solutions containing 0.001 g. per 100 cc. in the case of Butter Yellow, and 0.004 g. per 100 cc. in the case of the others, indicated that the absorptions may be assumed to be proportional to the concentrations within the ranges in which they may be accurately measured by the apparatus employed.

The measurements were made at 23° C. Readings made at higher and lower temperatures showed that a variation of 3° affected the reading less than 1 per cent. Except with Butter Yellow, the effect appeared to be negligible.

The effect of variations in the strength of the alcohol used as solvent was also determined. Fortunately the absorption at 0.436μ does not vary greatly with changes in the water concentration in case of Yellow AB and Yellow OB and may be considered as practically constant with alcohol ranging from 90 to 95 per cent by weight. The effect of water in the solvent is more marked with the other two dyes, the solutions being redder and the absorption lower at 0.436μ with increasing water content.

The ordinary method of calculating the amounts of each of the components of a known binary mixture of dyes from the extinction coefficients determined at two points in the spectrum has been tried for the analysis of mixtures of Yellow AB and Yellow OB. The absorption curves of these substances are so similar in form and position, however, that the method gives very inaccurate results unless the measurements are made with unusual care. The extinction coefficients for concentrations of 0.02 g. per liter at 0.492μ are approximately 0.66 for Yellow AB and 0.74 for Yellow OB. Measurements made in the spectral region at or near 0.492μ are suitable for use in connection with those taken at 0.436μ, but as no source of strong monochromatic light was available for making such measurements it has been necessary to employ a white light source (Mazda lamp) and to avoid the difficulties arising from the use of non-homogeneous light by carrying through standard solutions or mixtures at the same time. In some cases these standard solutions were used instead of the pure solvent in the comparison cavity of the double cell.

The relative difference in the specific absorption of the two dyes appears to be considerably greater at 0.546μ (the strong green line of the mercury arc) than in the blue and violet regions of the spectrum. Measurements made at this point, using solutions in 93 per cent alcohol containing 1.00 g. per liter of the preparations already mentioned, gave values of 1.05 and 1.53 for Yellow AB and Yellow OB, respectively.

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[1] A full discussion of the development and use of spectrophotometric methods of analysis is given in the handbook by G. and H. Kruess, "Kolorimetrie und Quantitativ Spektral-Analyse," Hamburg, **1909**.

[2] *J. Assoc. Off. Agr. Chem.*, **2** (1916), 164.

[3] The extinction coefficient found for Sudan I (0.002 g. per 100 cc.) in absolute alcohol in white (arc) light, 0.473μ to 0.480μ, was 1.18, a value about 40 per cent higher than that given at 0.436μ under the conditions described in this paper. With the other dyes the differences were much less.

Such data can scarcely be applied to the estimation of the dyes because of the relatively great effect of colored impurities on the absorption constants in the regions where the transmission is high. With commercial samples, the absorption at 0.546μ has been considered of some value as an index to their grade.

Sudan I and Butter Yellow can be more readily determined spectrophotometrically when in admixture with each other or with one of the dyes just discussed, the extinction coefficients in concentrations of 0.02 g. per liter at 0.492μ being approximately 1.17 for Sudan I and 0.26 for Butter Yellow. Butter Yellow has also the convenient property of becoming red (giving high absorption at 0.546μ) with small amounts of strong acids. However, these dyes may be readily separated and estimated directly, and this procedure has been preferred. Although the wave length of the blue light for which Yellow AB and Yellow OB show equal absorption is slightly greater than 0.436μ, that of the mercury line, the extinction coefficients are so nearly the same for this radiation that the mean of their values may be used for calculating the sum of the two dyes in a mixture free from other coloring matters without introducing an error exceeding one-seventieth of the value found.

COLOR TESTS FOR YELLOW AB AND YELLOW OB

In conclusion, a few properties which have been applied as color tests for the dyes may be mentioned. Yellow AB and Yellow OB readily condense with formaldehyde in presence of strong acids or acetic anhydride, the Yellow AB mixtures being much redder in shade.[1] Five cc. of a gasoline solution containing 0.001 g. dye per 100 cc. may be shaken in a test tube with 5 cc. of a mixture of 1 part commercial 40 per cent formaldehyde solution and 4 parts acetic anhydride. The coloring matters are extracted by the anhydride, Yellow AB and *p*-tolueneazo-β-naphthylamine forming solutions that become red in a few seconds. Yellow OB and *m*-xyleneazo-β-naphthylamine give orange solutions under the same conditions.

Yellow AB and Yellow OB form in fuming sulfuric acid (about 20 per cent sulfur trioxide) violet-blue solutions which slowly become red on standing. *p*-Tolueneazo-β-naphthylamine and *m*-xyleneazo-β-naphthylamine dissolve with a red color. Solutions in acetic anhydride containing 0.01 to 0.001 per cent of any of these four dyes become bluish red on the addition of a few drops (or 0.02 volume) of concentrated sulfuric acid, changing in 2 or 3 min. to a clear yellow.

SUMMARY

I—Attention is called to a source of error in the use of acid immiscible-solvent mixtures for separating oil-soluble food colors.

II—A description is given of the use of light gasoline and dilute sulfuric acid of different concentrations for detecting foreign dyes in commercial Yellow AB and Yellow OB colors.

III—Experiments are described indicating methods for the quantitative separation of mixtures of the dyes.

IV—Spectrophotometric data are given which have been applied to the quantitative estimation of Yellow AB, Yellow OB, Butter Yellow, and Sudan I.

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[1] Goldschmidt and Poltzer, *Ber.*, **24** (1891), 1000, condensed benzeneazo-β-naphthylamine by heating with formaldehyde at 140° C., forming phenyldihydro-β-naphthotriazine. With acetaldehyde the reaction began at ordinary temperature on mixing the substances. It has been observed here that the reaction between formaldehyde and Yellow AB (or Yellow OB) takes place very readily when a concentrated alcoholic solution of the substance is treated with sufficient hydrochloric acid to form the salt of the dye base. The colorless triazine derivative forms the chief reaction product under these conditions and is readily separated from the mixture. If a 0.002 per cent solution of Yellow AB in ordinary 95 per cent alcohol is treated with one-fourth its volume of concentrated hydrochloric acid or 18 *N* sulfuric acid, and neutralized, it will be found that the hue of the mixture does not return to yellow but remains orange-red, most of the dye having undergone condensation with substances present in the solvent.

DETERMINATION OF SULFUR FORMS IN COAL[1,2]

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An accurate method for determining each form of sulfur in coal would be useful, as indicating how much of the sulfur-containing material could be removed from the coal by washing processes, what effect the sulfur had on the heating value of the coal, how the various sulfur forms behaved during the coking and gas making processes, and other facts of interest to coal technologists.

HISTORICAL

Iron pyrite has been known for a great many years as one of the constituents of coal, and there has also been fairly good evidence of the presence of sulfur in organic combination. The first method proposed for the determination of these two forms was by means of sodium hypobromite.[3] The supposition was that the hypobromite dissolved the pyrite and sulfates without affecting the organic sulfur, but it was later shown[4] that some of the organic sulfur was brought into solution by this method.

In a method used in recent years the total iron in the coal, minus any water-soluble iron that may be present, is considered to be combined as pyrite. From this value is calculated the sulfur existing as pyrite. Any sulfur present as sulfate may be determined by a simple extraction with dilute acid. The pyritic sulfur plus the sulfate sulfur when subtracted from the total sulfur gives that organically combined, provided no other form exists in the coal. This method must be regarded as a rough approximation only, since it disregards the presence of iron silicate.

A method based on a gravity separation was devised in 1914 by Messrs. A. C. Fieldner and F. D. Osgood, of the Bureau of Mines. The coal was separated into float and sink fractions by the use of zinc chloride solution of 1.35 specific gravity. The sulfur in the heavy portion was considered as pyrite and that in the light fraction organic sulfur, after calculating the small amount of iron in this latter fraction to pyrite. This method was somewhat approximate, but its application indicated that organic sulfur was present in most coals to a much larger extent than had been generally supposed.

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[1] Published by permission of the Director of the U. S. Bureau of Mines.

[2] Presented at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

[3] T. M. Drown, *Chem. News*, **43** (1881), 89.

[4] Ferd. Fischer, *Z. angew. Chem.*, **12** (1899), 764.

Coal pyrite has been determined very recently by a roasting method,[1] in which the soluble iron compounds were washed out of the coal and the residue strongly ignited, to convert the pyrite to iron oxide. This oxide was extracted and determined, and the pyrite calculated. It would seem, however, that there might be a possibility of the iron oxide reacting with other ash constituents during the ignition to form silicates.

An accurate analytical method has, within recent years, been developed for the systematic analysis of sulfur forms in coal.[2] On testing out this method it has given good results with the coals analyzed, most of which were Illinois coals. The purpose of the present investigation is to extend the method to a variety of coals from entirely different fields, to make a thorough study of the sulfur forms present, and devise any modification of the method necessary in certain cases.

EXPERIMENTAL METHODS

The methods of analysis were practically the same as those used by Powell and Parr, but modified at certain points; for portions of the analysis, recommendations have been made, which it is thought will render the method more applicable to routine analytical procedure.

TOTAL SULFUR—Total sulfur determinations were made on each coal by the sodium peroxide method as used by Powell and Parr. The results were very irregular, and blank determinations on the sodium peroxide showed large quantities of sulfur which were not constant for different portions of the same batch. Furthermore, the nickel crucibles were attacked by the hot alkaline fusion to such an extent that some nickel was occluded by the barium sulfate in the final precipitation.

These difficulties led to the adoption of the Eschka method for sulfur in coal. This was used not only in the determination of total sulfur, but also for the sulfur in coal residues throughout the investigation. The percentage of total sulfur in the coal, as well as that of the different sulfur forms, is calculated on the basis of the air-dry coal.

SULFUR AS SULFATE—The analysis for sulfate was performed in exactly the manner used by Powell and Parr. Five-gram samples of the coal were extracted with 300 cc. of 3 per cent hydrochloric acid for 40 hrs. The beakers in which the extraction took place were kept over a water bath, at a temperature of about 60° C. The contents were filtered, and the filtrate was analyzed for iron by the Zimmerman-Reinhardt potassium permanganate titration method and for sulfur by the usual barium sulfate precipitation.

Later experiments have indicated that the extraction time may be shortened considerably without appreciably affecting the determination. If the finely powdered coal is boiled with concentrated hydrochloric acid diluted to twice its volume, complete extraction of the sulfates is secured in 15 or 20 min. Although pyrite is slowly decomposed under these conditions, the extraction time is so short that the quantitative results are not affected.

SULFUR AS PYRITE—For the pyrite analysis, one-gram samples of the coal were allowed to stand with 80-cc. portions of dilute nitric acid (sp. gr. 1.12) for 2 or 3 days at room temperature. Twenty-four hours is probably sufficient for this extraction although a longer time does no harm. If a shaking machine is available, the extraction time can be cut down to 1 or 2 hrs.

The extract was filtered off, and the nitric acid was evaporated on the water bath. The residue from this evaporation was taken up in hydrochloric acid and analyzed for iron and sulfur by the methods just mentioned.

The iron obtained in the nitric acid extract represented the iron which was extracted by the hydrochloric acid plus the iron combined as pyrite. Therefore, the pyritic iron could be figured by the difference between the two iron determinations. The sulfur in the nitric acid extract represented the sulfate sulfur, which had been determined previously by hydrochloric acid treatment, plus the sulfur combined as pyrite. Also, if the dilute nitric acid were dissolving any of the organic sulfur, this would appear in the extract. The question as to whether any of the organic sulfur was being dissolved could be answered by comparing the percentage of pyritic iron with what was presumably the percentage of pyritic sulfur, as obtained by subtracting the percentage of sulfur found in the hydrochloric acid extract from that found in the nitric acid extract. If the pyritic iron and the sulfur were in the exact proportions to form FeS_2, the nitric acid was a selective solvent for pyrite in that particular coal. If the sulfur were in excess, however, the indications would be that the organic sulfur of that coal was being attacked by the dilute nitric acid. By means of these calculations the accuracy of the method for pyritic sulfur was checked.

SULFUR IN ORGANIC COMBINATION—In ordinary commercial practice, the organic sulfur would be determined by subtracting the sum of the two inorganic forms from the total sulfur. In the present investigation it was necessary to prove that this remainder was organic.

The amount of sulfur in organic combination was determined by much the same means as those used by Powell and Parr. The phenol-soluble type of organic sulfur was calculated from the difference between the total sulfur content of the coal and the sulfur content of the coal residue after phenol extraction.

The extraction of the coal by phenol was carried out in an oven at a constant temperature of 150° C. Air condensers were so arranged that the vaporized phenol would be carried back into the extraction flasks. One-half gram samples of coal and 25 cc. of phenol were placed in the flasks, and the extraction was allowed to proceed for 20 hrs. The contents were filtered through a porcelain Gooch crucible, and thoroughly rinsed with alcohol and ether. The entire asbestos mat, with its covering of coal residue, was ground up with the Eschka mixture, and the sulfur determination run in the usual manner. As stated before, the phenol-soluble organic sulfur was obtained by difference.

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[1] J. P. Wibaut and A. Stoffel, *Rec. trav. chim.*, 38 (1919), 132.

[2] A. R. Powell with S. W. Parr, University of Illinois Engineering Experiment Station, *Bulletin* 111 (1919), 10.

TABLE I—SOURCES, PROXIMATE ANALYSES, AND CALORIFIC VALUES OF COALS

NUMBER	SOURCE			PROXIMATE ANALYSIS[1]					CALORIFIC VALUE	
	State	County	Coal Bed	Moisture	Volatile Matter	Fixed Carbon	Ash	Sulfur	Cal.	B. t. u.
23066	Pennsylvania	Butler	Upper Freeport	2.04	33.11	56.36	8.49	1.21	7450	13410
18847	Pennsylvania	Allegheny	Pittsburgh	1.58	38.72	54.95	4.75	1.72	7901	14222
20507	West Virginia	McDowell	Pocahontas No. 3	0.40	22.88	70.47	6.25	0.56	8133	14639
21308	Kentucky	Letcher	Elkhorn	1.67	37.78	56.57	3.98	0.71	7910	14238
21100	Tennessee	Morgan	Coal Creek	0.75	39.05	52.40	7.80	4.25	7821	14078
27224	Kansas	Cherokee	Cherokee	1.73	34.90	55.14	8.23	3.06	7559	13606

[1] All samples were in an air-dry condition.

TABLE II—ANALYSIS FOR PYRITIC SULFUR IN COALS BY EXTRACTION, AND BY CALCULATION FROM IRON

	PER CENT AIR-DRY COAL											
LABORATORY NUMBER	23066		18847		20507		21308		21100		27224	
Total sulfur, as determined	1.21		1.72		0.56		0.71		4.25		3.06	
Sulfur soluble in dilute HNO₃	0.54		1.02		0.09		0.17		2.46		2.31	
Sulfur soluble in dilute HCl	0.07		0.23		0.01		0.04		0.71		0.32	
Pyritic sulfur, direct extraction		0.47		0.79		0.08		0.13		1.75		1.99
Iron soluble in dilute HNO₃	0.52		1.05		0.43		0.32		2.48		2.25	
Iron soluble in dilute HCl	0.14		0.37		0.35		0.20		0.94		0.49	
Pyritic iron, direct extraction	0.38		0.68		0.08		0.12		1.54		1.76	
Pyritic S, calculated from Fe		0.44		0.78		0.09		0.14		1.76		2.01
Difference between pyritic sulfur values by two methods		0.03		0.01		0.01		0.01		0.01		0.02

The phenol-soluble material is known to be organic because of its lack of ash.

The so-called "humus" type of organic sulfur—that very stable portion which is not extracted by phenol—was determined directly by a method differing slightly from that used by Powell and Parr. The residues from the dilute nitric acid extraction, previously described, were used for these experiments, since all the inorganic sulfur had been removed and all of the organic sulfur was present. In most cases, particularly where little is present, the phenol-soluble sulfur will respond to the treatment which is given the more stable humus organic sulfur. The following method was accordingly used for the total organic-sulfur determination. In the case of only one coal, where the phenol-soluble sulfur was high, was it necessary to extract first with phenol, then with dilute nitric acid to remove the inorganic sulfur, and to finish the analysis for the humus organic sulfur by itself.

It was found that the residue from dilute nitric acid extraction did not readily dissolve in ammonia, so this residue was further treated with concentrated nitric acid. The nitric acid was then evaporated off on the water bath, leaving a residue readily soluble in ammonia. In the case of one coal, a semi-bituminous coal from the Pocahontas field, three treatments with nitric acid, followed each time by evaporation on the water bath, were necessary to digest sufficiently the coal for the alkaline solution.

The residues were treated with 25 cc. of concentrated ammonia and allowed to stand for some time. They were then filtered through an ordinary filter paper, the filtrations requiring about one week on account of the colloidal nature of the solutions. Previous research has shown that this alkali-soluble material was almost ash-free, and, therefore, organic in nature. Most of the ash of the coal was left on the filter.

The dark brown, colloidal solution was evaporated to dryness on the water bath, and the sulfur in the residue was determined by the Eschka method. This, then, gave the total organic sulfur content of the coal by a direct procedure, unless the coal had previously been extracted with phenol, in which case the above process gave the humus type of organic sulfur by itself.

This procedure indicated whether the methods of analysis for the various forms of sulfur in the coal were accurate, and the only question left was as to the possible existence of some other form of sulfur in the particular coal studied. This was easily determined by comparing the sum of the percentages of the forms of sulfur for which analyses had been run with the total sulfur percentage of the coal.

DESCRIPTION OF COALS

In choosing coals for these experiments it was necessary to select a small number only, since the detailed study required a good deal of time for each coal. It was preferable to take samples which had stood some time, so that there would be an appreciable amount of sulfate present, as in freshly mined coal this form of sulfur is generally very small in quantity. Table I gives a detailed description of the source of each coal used, its proximate analysis, and its calorific value.

RESULTS OF EXPERIMENTS

The first set of experiments dealt simply with the determination of the sulfate and pyritic forms of sulfur. The data obtained from these experiments are given in Table II.

It will be noticed that the analytical results for pyritic sulfur in all six of the coals check up to within a very reasonable experimental error. Some trouble was encountered with Coal 21,100, in that the sulfur extracted by dilute nitric acid was larger than the sulfur calculated from pyritic iron. In order to do away with this discrepancy, it was found necessary to extract the more unstable phenol-soluble sulfur before making the nitric acid extraction. Since it would not be practical to perform this phenol extraction for every analysis, the pyritic sulfur as calculated from the iron should be the value used for rapid technical work.

TABLE III—SUMMARY OF ANALYSES FOR SULFUR FORMS IN COAL

NUMBER	23066	18847	20507	21308	21100	27224
Pyritic sulfur	0.47	0.79	0.08	0.13	1.75	1.99
Sulfate sulfur	0.07	0.23	0.01	0.04	0.71	0.32
Humus organic sulfur	0.50	0.46	0.44	0.42	1.01	0.39
Phenol-soluble organic sulfur	0.12	0.20	0.02	0.09	0.77	0.32
TOTAL	1.16	1.68	0.55	0.68	4.24	3.02
Total by direct analysis	1.21	1.72	0.56	0.71	4.25	3.06
Difference between totals	0.05	0.04	0.01	0.03	0.01	0.04

Table III gives in a condensed form the results of analyses for the different forms of sulfur and a comparison of their total with the total sulfur of the coal.

It can be seen from this table that the sum of the different analyses checks very closely with the total sulfur in the case of each coal. There can be no doubt, therefore, that all the sulfur of these coals has been accounted for in the four forms of pyrite, sulfate, and the two forms of organic sulfur.

CONCLUSIONS

1—The method of Powell and Parr for sulfur forms in coal gives correct and accurate results, as proved by experiments on a variety of coals from different regions.

2—The method may be used as originally outlined, but for rapid routine work the following changes are suggested:

(*a*) After the sulfate and pyrite determinations are completed, the organic sulfur may be reckoned from the total sulfur by difference.

(*b*) The extraction of sulfates may be completed in a few minutes by boiling with hydrochloric acid (sp. gr. 1.12) rather than by slow extraction with the very dilute acid. The boiling acid does not decompose pyrite to any appreciable extent.

(*c*) The extraction of pyrite by dilute nitric acid may be completed in an hour or two by the use of a shaking machine.

(*d*) Dilute nitric acid will extract small amounts of the unstable phenol-soluble form of organic sulfur from certain coals. To avoid this error in laboratory determinations, it is recommended that pyritic sulfur be calculated from the pyritic iron value.

(*e*) The dilute nitric acid not only extracts pyrite quantitatively, but also the same iron and sulfur which is taken into solution by dilute hydrochloric acid. For this reason, samples intended for dilute nitric acid extraction need not be extracted with hydrochloric acid first.

3—Semi-bituminous coals and the harder varieties of bituminous coals must be digested for a long time with concentrated nitric acid before the organic matter will become completely soluble in ammonia.

4—The Eschka method is preferable to the sodium peroxide method for the determination of sulfur in coal and coal residues, unless the sodium peroxide used has a low and constant sulfur content.

ACKNOWLEDGMENTS

The author wishes to express his appreciation and gratitude for many valuable suggestions to Mr. A. C. Fieldner, supervising chemist, under whose general direction this investigation was conducted, and to Mr. E. A. Holbrook, superintendent, Pittsburgh Experiment Station, Bureau of Mines, and to Professor S. W. Parr, University of Illinois.

THE DIFFUSING POWER OF PIGMENTS[1]

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The methods ordinarily employed for the determination of the covering power of pigments are highly unsatisfactory, because most of them give relative values only, involve a difficult technique, or use complicated apparatus. This laboratory has developed a new testing method for pigments which, while it does not measure covering power, is simple in both technique and apparatus and gives results expressed in absolute figures, which can be duplicated by different observers in different laboratories.

If a finely divided solid be suspended in a suitable fluid, light passing through the suspension is diffused, producing a "ground glass" effect. The diffusion increases greatly with the number of particles, and is probably nearly proportional to the total number of particles, and relatively independent of their size. This diffusion is the basic principle employed in every turbidimeter; that is, some object is observed through the suspension, and the thickness of suspension just required to blur the object is measured.

In the present method the filament of an incandescent lamp is observed, and the thickness of pigment suspension needed to completely blur the filament is determined. It should be noted that the suspension does not shut off the light from the filament. It is, however, diffused to such a degree that the outline of the filament is no longer perceptible. The depth of suspension just necessary to obscure the filament can be determined with remarkable precision.

That the phenomenon is not one of light absorption becomes especially evident on changing the brilliance of the filament. The depth of suspension necessary to obscure remains the same whether the filament be operated at a voltage so low that it is dull red, or at an excess voltage almost sufficient to burn it out. The amount of light observed is, of course, widely different in the two cases; but if a certain fraction of the light from the object is diffused, it becomes indistinct, although most of the light from it may reach the eye. The proposed method determines the thickness of suspension necessary to diffuse that critical fraction of light from the object which will render the object indistinct.

The pigment to be tested is suspended in a suitable fluid, and the suspension is maintained by any satisfactory method of stirring, such as using a stirring rod or blowing air through the liquid. The apparatus consists of a vertical cylinder of metal or glass, to which is cemented a plate glass bottom, plate glass being used to make sure that the two faces are absolutely parallel. The sides of the cylinder are preferably blackened, but this is not essential. The suspension, the pigment concentration of which is known, is poured into the cylinder until the filament of an incandescent lamp held just below the bottom can no longer be distinguished, and the depth of suspension is accurately noted.

It has been experimentally determined that the depth of suspension observed is inversely proportional to the concentration of the pigment. This means that the disappearance of the filament is determined by the amount of pigment per unit area of cross section of the cylinder, and is uninfluenced by the position of the pigment particles in the direction in which the light is traveling. It is this weight in grams required for each square centimeter of section which is measured. We prefer to report the reciprocal of this quantity, *i. e.*, the square centimeters of surface which one gram of pigment is capable of covering. This quantity is called the diffusing power of the pigment, and, while expressed in square centimeters per gram, it would be equally satisfactory if expressed in square feet per pound. As a measure of fineness it is probably even better to express the results on a volumetric basis, *i. e.*, as square centimeters per cubic centimeter of pigment, or square feet per cubic foot.

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[1] Presented at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920, and also before the Cleveland Section of the Society.

The diffusing power of a pigment is a function of the completeness with which it is dispersed in the fluid employed. In the investigation linseed oil has usually been used, the pigment ground by hand in a small amount of oil, and gradually diluted with more oil, till a suitable suspension was obtained. For most pigments the diffusing power becomes practically constant after a half hour's grinding. Only clear liquids should be used; bleached linseed oil, for instance, eliminates any effect of turbidity of the oil itself. That the diffusing power increases with time of grinding is shown by Table I.

TABLE I—CARBON BLACK IN LINSEED OIL

Time of Grinding Minutes	Diffusing Power Sq. Cm./G.
0	343
10	1416
20	1760
30	2220
45	2180

Table II indicates that the results are independent of the concentration of the pigment in the diffusing liquid.

TABLE II—WHITE LEAD IN LINSEED OIL—NO GRINDING

Concentration Gm./1000 Cc. Oil	Diffusing Power Sq. Cm./G.
0.247	224
0.269	229
0.319	213
0.391	207
0.449	206
0.484	218
0.628	199
0.690	204
0.834	224
1.21	212
1.45	209
1.53	198

The diffusing power is profoundly influenced by the dispersing liquid employed; thus for a certain white lead dispersed in linseed oil without grinding, a diffusing power of 212 sq. cm. per gram was obtained, whereas the same pigment dispersed in water in the same way gave a diffusing power of only 104.

Diffusing power must not be confused with covering power, nor with the so-called "hiding power."[1] The covering power of pigments is unquestionably influenced by their light absorption capacity, a factor which is entirely eliminated in the determination of diffusing power. The latter is, however, a very direct measure of the fineness of a given pigment as suspended in the liquid employed.

Everyone experienced in the determination of covering power is familiar with the difficulties which develop in testing colored pigments. This method of determining diffusing power entirely eliminates such difficulty. The color of the pigment has apparently no influence on the result obtained. The method can be applied to all pigments, whether white, black, or colored, independently of shade, gloss, and other factors which so seriously affect the determination of covering power. Table III shows the diffusing power of samples of certain of the more important pigments.

TABLE III—PIGMENTS GROUND IN LINSEED OIL

PIGMENT	Diffusing Power Sq. Cm./G.
White lead	260
Carbon black	2200
Lamp black	1830
Red iron oxide	348
Red lead	137
Zinc oxide	560
Whiting	295
Barytes	170
Lithopone	560

SUMMARY

The diffusing power of pigments can be determined by measuring the weight of pigment per unit of cross sectional area necessary to obscure objects behind a suspension of the pigment, the result being expressed as square centimeters per gram or square feet per pound. The determination can be carried out in simple apparatus, and results can be checked with accuracy. It is believed that the diffusing power is the most satisfactory measure of the fineness of a pigment, and as such is of obvious interest and value to the rubber trade.

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[1] A. H. Pfund, "The Hiding Power of White Pigments and Paints," *J. Frank. Inst.*, **188** (1919), 675.

LABORATORY AND PLANT

THE DETERMINATION OF THE SPECIFIC HEAT OF HEAVY MINERAL OILS[1]

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Because of unaccountable heat losses in the oil circulating system of a certain plant, it recently became advisable to determine the specific heats of several high flash test, heavy mineral oils. It was essential to ascertain the mean specific heat for short temperature intervals at relatively high temperatures, principally between 150° to 250° C. The literature on the specific heat of liquids at elevated temperatures appears to be very meager.

For the particular specific heat determinations in question it was, therefore, necessary to devise on short notice a method which would give fairly accurate results and be available later for plant control work. It is believed that the procedure developed can be safely recommended as meeting these requirements. The method depends upon the direct determination of the electrical energy required to heat a definite mass of oil over a given temperature range. The apparatus is readily assembled from the equipment of any first-

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[1] Presented at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

class laboratory; the determinations can be carried out rapidly and with ease; they can be made at any temperature below the point where vaporization of the sample causes an appreciable error; and the uniformity and accuracy of the results are satisfactory for the calculation of heat transference data in oil circulating systems. Since this work was completed an article[1] has appeared describing an apparatus somewhat similar to that used by us, although the method of carrying out the determination is not the same as the one we adopted. At the time that this method was being tried, the method of mixtures was used with the same oils, but the results obtained by the electrical method were more uniform and, it is believed, more accurate. In those cases where the least difficulty was met in using the method of mixtures, the results by the two methods agreed very closely.

DESCRIPTION OF APPARATUS

The apparatus finally adopted consisted of a calorimeter equipped with an electrical resistance heating coil, a stirrer, and a thermometer. The calorimeter was a one-quart, vacuum-jacketed, glass vessel, 2.5 in. in diameter, and 11.5 in. deep, enclosed in a copper jacket. (Sold under the name of "Thermos Fruit Jar.") The heating unit was a coil made of 24 in. of No. 24 B. and S. (0.020 in. diameter) "Climax" resistance wire, slipped over a bent glass rod, and soldered to copper leads. The stirrer was a glass rod with two blades, and was operated at a constant speed by a water motor. The copper leads, the stirrer, and the thermometer were passed into the calorimeter through a tightly fitting cork stopper. The current was obtained from a generator having a capacity of 8.5 volts and 75 amperes, the exact values of which were read from instruments placed in the line.

DETAILS OF ELECTRICAL METHOD

The details of the method were as follows: 250 g. of oil were placed in the calorimeter, the stopper fitted tightly in place, the stirrer started, and the current turned on. The temperature of the oil and calorimeter was allowed to rise slowly to the lowest point of the temperature range over which the specific heat was to be determined. Beginning at this point, and continuing over the desired range, possibly 20° C., readings were made of the temperature, the voltage, and the amperage, at half-minute or one-minute (exact) intervals. When the temperature of the system reached the maximum point of the range, the current was cut off, and the system allowed to cool with the agitator still running continuously. During the cooling period, the temperature was noted at 5 or 10 min. intervals (time accurately noted) over the range through which the system had previously been heated, the radiation rate (temperature drop per minute) being thus obtained directly.

The water equivalent of the calorimeter was found by the method just described for determining the specific heat of an oil, and with this, after making the proper correction for the emergent stem of the thermometer, all the essential data were available for the calculation of the specific heat of the oil over any particular range.

It should be noted that the energy imparted to the system by the mechanical stirring, and the heat required to raise the temperature of the calorimeter are automatically allowed for in making a determination. Since the agitator runs continuously during the entire process, the heat it imparts to the system during the cooling period is practically the same per unit of time as during the heating period, and allowance for agitation energy may, therefore, be eliminated.

To check up the results, the specific heat of aniline was determined by this method, and found to be 0.508 at 55° C., a figure which agrees closely with the values found in the literature.[1]

EXPERIMENTAL DATA

As an example of the individual readings made in the course of a single determination, a copy of a "log sheet" is given in Table I.

TABLE I—SPECIFIC HEATS AT 120°–140° C.

During Heating Period

Time Min.	Volts (V)	Amp. (A)	Temp. ° C.	Temp. Diff. ° C.	Time Diff. Min.	Temp. Diff. per Min. (t)
0	7.40	1.64	120.0	...	..	....
2	7.50	1.68	121.8	1.8	2	+0.90
4	7.60	1.70	123.5	1.7	2	+0.85
6	7.58	1.71	125.3	1.8	2	+0.90
8	7.57	1.67	127.0	1.7	2	+0.85
10	7.40	1.65	128.7	1.7	2	+0.85
12	8.05	1.80	130.4	1.7	2	+0.85
14	8.38	1.85	132.6	2.2	2	+1.10
16	8.30	1.84	134.8	2.2	2	+1.10
18	8.30	1.82	136.9	2.1	2	+1.05
20	8.31	1.83	139.0	2.1	2	+1.05
22	8.30	1.82	141.0	2.0	2	+1.00
	Av., 7.89	1.75				+0.954
During Cooling Period						
0	..	..	142.4	...	..	..
10	..	..	139.5	...	10	—0.29
20	..	..	136.7	...	10	—0.28
30	..	..	134.0	...	10	—0.27
40	..	..	131.4	...	10	—0.26
50	..	..	128.8	...	10	—0.26
60	..	..	126.4	...	10	—0.24
70	..	..	124.0	...	10	—0.24
80	..	..	121.7	...	10	—0.23
87.5	..	..	120.0	...	7.5	—0.23
Average radiation—degree drop per min. (r)................						—0.26

CALCULATION OF EXPERIMENTAL RESULTS

The equation by means of which the calculation of specific heat is made is derived as follows:

$V \times A \times 60 \times 0.239$ = Heat input in calories per min., where V = average voltage, A = average amperage over the desired temperature range, 60 = seconds, converting watts to joules, and 0.239 = calories per joule.

Let C = heat capacity of oil
e = water equivalent of calorimeter, including stirrer, etc.
$t + r$ = corrected temperature rise per min. which includes t (actual rise ° C. per min.) and r (radiation ° C. per min. from cooling curve)

$$V \times A \times 0.239 = (C + e)(t + r)$$

or
$$C = \frac{V \times A \times 60 \times 0.239}{t + r} - e.$$

If W = weight of oil, then

$$\text{Sp. Ht.} = \frac{C}{W} = \frac{V \times A \times 60 \times 0.239}{W(t + r)} - \frac{e}{W}.$$

Substituting in the equation the values from Table I, together with the value of 27.5 for the water equivalent of the calorimeter and 250 for weight of oil used, the following result is obtained for the temperature range of 120° to 140° C.:

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[1] Paul Pascal and Garnier, *Bull. soc. chim.*, [4] **27–28** (1920), 8.

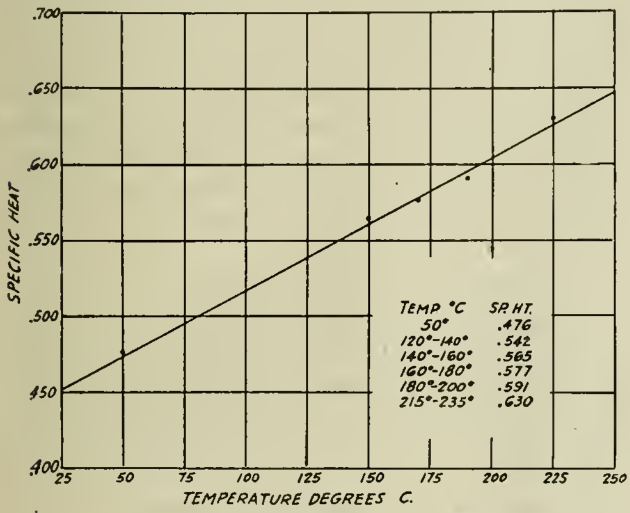
[1] Landolt and Börnstein's Tables, p. 174-*a*.

$$\text{Sp. Ht.} = \frac{7.89 \times 1.75 \times 60 \times 0.239}{250\,(0.954 + 0.26)} - \frac{27.5}{250} = 0.543$$

The resulting figures for the specific heats of the mineral oil tested, as calculated by this method, are as follows:

Temperature ° C.	Specific Heat
50	0.476
120–140	0.543
140–160	0.565
160–180	0.577
180–200	0.591
215–235	0.630

These values are shown graphically in the accompanying curve. It will be noted that the specific heat increases with rise in temperature and is practically a straight line function of the temperature. From this curve the specific heat at any temperature may be closely approximated.



Specific Heats of Heavy Mineral Oil as Determined by the Electric Method

OPTIONAL METHODS. FOR RADIATION CORRECTION

Two other methods for finding the cooling or radiation correction were investigated. The more important of these consisted in raising the temperature of the oil to the desired point by means of the resistance coil, then, by the use of the rheostat, cutting down the voltage and the current to the point where the energy input was just sufficient to overcome the radiation and to hold the oil and calorimeter at a fixed temperature. The radiation correction for any temperature range was thus obtained in terms of the heat in calories per minute required to hold the system at the middle point of the range. The values for the radiation correction as determined by this method, and by still another procedure which depended upon the rate of cooling at the beginning and end of the temperature period, agreed very closely.

The log sheets shown in Tables II and III are records of the data taken during a determination of the specific heat of the same oil covered by Table I but at a higher temperature. The radiation correction was obtained by measuring the electrical energy required to hold the temperature of the calorimeter and oil constant at the middle point of the range for which the average specific heat was being determined, as shown in Table III.

Table II—Log Sheet of Instrument Readings Made in Determination of Specific Heat for the Range 215° to 235° C.

Time Min.	Volts (V)	Amp. (A)	Temp. ° C.	Time Diff. Min.	Temp. Diff. ° C.	Temp. Diff. per Min. (t)
			Heating up from 215°–225° C.			
..	..	..	215.0	..	...	..
2	8.05	1.71	216.0	2	1.0	0.50
4	8.15	1.72	217.0	2	1.0	0.50
6	..	..	218.0	2	1.0	0.50
8	8.18	1.72	219.0	2	1.0	0.50
10	8.22	1.74	220.0	2	1.0	0.50
12	8.17	1.72	221.0	2	1.0	0.50
14	8.23	1.73	221.9	2	0.9	0.45
16	8.18	1.72	222.9	2	1.0	0.50
18	8.13	1.71	223.8	2	0.9	0.45
20	8.14	1.71	224.7	2	0.9	0.45
			Heating up from 225°–235° C.			
34[1]	7.40	1.53	225.9	2	0.7	0.35
36	8.28	1.75	226.5	2	0.6	0.30
38	8.14	1.72	227.4	2	0.9	0.45
40	8.02	1.70	228.4	2	1.0	0.50
42	8.10	1.69	229.3	2	0.9	0.45
44	8.03	1.67	230.1	2	0.8	0.40
46	7.93	1.65	230.9	2	0.8	0.40
48	7.93	1.65	231.6	2	0.7	0.35
50	7.84	1.64	232.3	2	0.7	0.35
52	7.83	1.64	233.0	2	0.7	0.35
54	7.75	1.63	233.6	2	0.6	0.30
56	7.71	1.63	234.2	2	0.6	0.30
$59^1/_3$	7.71	1.63	235.2	3.33	1.0	0.30
	Av., 8.00	1.68				0.42

[1] System held at 225.2° C. for 12 min. for radiation correction.

Using the values 6.17 volts and 1.29 amperes (Table III), which are the average voltmeter and ammeter readings corresponding to the heat input required to maintain the temperature of the system at 225.2° C., the radiation correction is found to be 114.2 calories per minute. This figure, R, is the actual energy input in calories per minute as derived from the equation:

$$V' \times A' \times 60 \times 0.239 = R$$

Substituting in the equation

$$\text{Sp. Ht.} = \frac{(V \times A \times 60 \times 0.239) - R}{W \times t} - \frac{e}{W}$$

the values $R = 114.2$, $V = 8.00$, $A = 1.68$, $t = 0.42$ from Table II, $W = 250$, the weight of oil used, and $e = 27.5$, the water equivalent of the calorimeter, we obtain for the temperature range 215° to 235° C. an average specific heat of 0.637. This value is 0.007 higher than that determined for the same oil over the same temperature interval in a duplicate run in which the radiation correction was derived from a "cooling curve" as in the method first described.

Table III—Log Sheet of Instrument Readings Made in Determination of Radiation Correction at 225.2° C.

Time Min.	Volts (V′)	Amp. (A′)	Temp. ° C.	Time Diff. Min.	Temp. Diff. ° C.
1	6.21	1.35	225.2	1	0.0
2	6.40	1.35	225.2	1	0.0
3	6.30	1.35	225.2	1	+0.1
4	6.25	1.30	225.3	1	0.0
5	6.22	1.31	225.3	1	0.0
6	6.20	1.30	225.4	1	+0.1
8	5.95	1.26	225.3	1	—0.1
8	6.00	1.25	225.3	1	0.0
9	5.90	1.24	225.2	1	—0.1
10	5.90	1.22	225.2	1	0.0
11	6.00	1.25	225.2	1	0.0
12	6.00	1.28	225.2	1	0.0
	Av., 6.17	1.29	225.2	1	0.0

The second method for determining the radiation correction is considerably quicker than that depending on the rate at which the system cools down when the heating current is turned off. This is especially true where a series of specific heat measurements are to be made on the same oil at different temperatures, as no time need be lost in cooling and heating up again. Unfortunately, however, a sufficiently constant supply of electrical energy to hold the calorimeter and oil at a uniform temperature long enough to make the correction reliable is seldom available in a works laboratory.

CONCLUSIONS

The method described is believed to be a simple and satisfactory means of determining the specific heat of liquids, especially at high temperature. It is especially adaptable to plant control work and to laboratory investigations where rapid work and a fair degree of accuracy are required. At high temperatures, and over short temperature ranges the method as described is more accurate than any other of which the writers have knowledge. Accuracy of any desired degree can undoubtedly be obtained by refinements in temperature and electrical energy measurements, and obviously the more perfect the insulation of the calorimeter the larger the proportion of the total energy input consumed in actually raising the temperature of the oil.

THE APPLICATION OF THE THERMAL CONDUCTIVITY METHOD TO THE AUTOMATIC ANALYSIS OF COMPLEX MIXTURES OF GASES[1]

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In a previous paper[2] there was described an automatic electrical method for gas analysis depending upon thermal conductivity, and its application to the determination of certain constituents in various mixtures of gases was illustrated by a number of representative analyses. It is the purpose of the present paper to show how the method may be applied to a much greater variety of analytical purposes than was even suggested in the former paper. The examples are intended to illustrate numerous possible ways of employing the method for complex mixtures, rather than to point out specific applications which would be likely to have industrial importance. As in the previous paper, the numerical results were obtained under laboratory conditions with all accessory apparatus of excellent quality and in accurate adjustment. It does not follow that as good results would be obtained under plant conditions, particularly with a recorder. However, the three recorders actually installed in manufacturing plants have thus far given satisfactory results.

Before further applications are described in detail, it may be well to point out some of the characteristics of the method which favor or limit its usefulness.

Probably the principal limitation upon the usefulness of the method is the fact that we cannot calculate the significance of the indications obtained, but must, in every case, depend upon empirical calibration under conditions closely approximating those of actual service. This limitation makes the method of little or no use for the occasional examination of isolated samples of gas, especially samples of which the qualitative composition is not known.

The qualitative compositions of most gas mixtures of industrial importance are known, however; their variations in composition are more or less regular; and the probable limits of variation are also known approximately. For the purpose of observing or recording changes in the composition of such mixtures, the thermal conductivity method possesses a combination of advantageous features not possessed by other methods of analysis. Inasmuch as the thermal conductivity of a gas is independent of its pressure over very wide ranges of variation, it is not necessary to provide for the maintenance of the gas at a constant pressure. It has been found that the indications of the apparatus developed at the Bureau of Standards are practically unaffected by small variations in the rate of flow of the gas. These two facts make it possible to obtain a continuous, rather than an intermittent, record of gas composition, and enable us to employ several expedients, to be described later, which are of the utmost importance in dealing with complex mixtures. High sensitivity is secured with apparatus of small dimensions; consequently the time lag between changes in composition and the corresponding indications of the apparatus is quite small, even when the flow of gas is very slow. By the use of refined apparatus far greater sensitivity to variations in the composition of a mixture may be secured, and at less expense, than by any other well-known method.

COMPARISON OF METHODS OF GAS ANALYSIS

For the sake of conveying a more definite idea of the relative advantages of this method and several of the more familiar methods of analysis, under the conditions outlined above to which the thermal conductivity method is suited, a tabular comparison is made in Table I. This table represents the judgment of the authors, who have had some experience with all the types of apparatus listed, and relates to methods of observing, rather than of recording, analyses. Since the thermal conductivity method loses little of its accuracy or dependability when used with a recorder and is in other respects ideally suited to continuous operation, while the contrary is true of recording apparatus depending upon density or volumetric measure-

Table I—Relative Advantages of Various Methods of Observing Gas Composition[1]

	Method				
Desirable Characteristics	Thermal Conductivity	Interferometer	Density Balance	Direct Weighing	Chemical Separation and Volumetric Determination
Sensitivity	1	2	5	4	3
General applicability	3	2	5	4	1
Independence of physical conditions difficult to control	2	4	3	5	1
Independence of calibration	5	4	3	2	1
Time lag	1	2	3	5	4
Time required of observer	1	2	3	5	4
Fatigue of observer	1	5	2	3	4
Skill required of observer	1	4	3	5	2
Computation required	1	4	3	5	2
Probable error of observation due to personal equation	1	4	3	5	2
Amount of gas required	1	4	2	5	3
Probable cost of apparatus	3	4	2	5	1
Probable cost of continuous operation	1	4	2	5	3

[1] The method possessing the greater advantage is given the smaller number.

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[1] Published by permission of the Director of the Bureau of Standards.

[2] This Journal, 12 (1920), 359.

ment, it is at once apparent that this method makes possible a considerable advance over the older methods of recording gas analysis.

APPLICATIONS OF THERMAL CONDUCTIVITY METHOD

The thermal conductivity method is always essentially a comparison of the thermal conductivities of two gases. The method of making this comparison was set forth in sufficient detail in the earlier paper. The present paper deals primarily with the question of what gases to compare in order to obtain useful data in a given case.

METHOD I. COMPARISON WITH A STANDARD GAS—Probably the simplest method of application of the thermal conductivity apparatus is the comparison of the mixture to be analyzed with a gas of known composition, called a "standard gas." This method is applicable to the following classes of gas mixtures:

(*a*) Mixtures containing only two components.

(*b*) Mixtures of two gas mixtures in each of which the proportion of various constituents is known to be constant. This class includes mixtures of a pure gas with mixtures of constant composition.

(*c*) Mixtures in which it is known that the constituent of interest has a conductivity widely different from the conductivities of the other constituents, all of which latter conductivities are known to be of nearly the same magnitude.

The determination of helium in mixtures of helium and nitrogen occurring in the later stages of the separation of helium from natural gas, and the determination of the relative proportions of hydrogen and nitrogen in the purified gases used in the synthetic ammonia process are examples of Class (*a*), which were cited in the earlier paper. Other easy and important applications to this class of mixtures are the determination of hydrogen in electrolytic oxygen and of oxygen in electrolytic hydrogen.

A good example of Class (*b*) is the determination of the proportions of natural gas, from each of two fields, which enters the helium plant at Petrolia, Texas. Both gases consist of mixtures of methane, nitrogen, ethane, and some higher hydrocarbons, with a small percentage of helium. The composition of each gas is quite constant, but the difference between the two is so great as to render changes in plant operation desirable when their relative proportions are changed. The relative proportions of the gases from the two fields have been successfully recorded for several months, in spite of the fact that the difference between their heat conductivities is approximately only one per cent of the difference between the conductivities of helium and nitrogen. The determination of hydrogen in air, which was reported in the previous paper, is an example of this class of determinations which is extremely easy and accurate.

Class (*c*) includes the determination of hydrogen in water-gas and in the mixture of nitrogen, hydrogen, and carbon monoxide existing at one stage of the synthetic ammonia process. The conductivities of nitrogen (0.524) and of carbon monoxide (0.499) lie very close together, while that of hydrogen (3.27) is relatively very great. The relative proportions of nitrogen and carbon monoxide therefore make little difference in the determination of hydrogen. The same relation is practically true in the case of the mixtures of helium, nitrogen, and methane existing at one stage of the helium extraction process, so that the helium content can be determined with considerable accuracy in spite of variations in the relative proportions of methane and nitrogen. The determination of the lifting power of balloon gas is another good example of this class of determination. The impurities likely to occur in hydrogen produced for balloon purposes, and also the gases of the atmosphere, including water vapor and carbon dioxide, all have relative effects upon the lifting power of the balloon gas which approximate their relative effects upon its thermal conductivity. This relation holds whether helium or hydrogen is used in the balloon.

Air and hydrogen have been found to be the gases most generally useful as the standard comparison gas; air is used when the mixture for analysis has a low conductivity, and hydrogen is compared with mixtures which have a high conductivity.

METHOD 2. COMPARISON OF THE GAS BEFORE AND AFTER A CHEMICAL REACTION—The determination of a constituent of a mixture of gases by the comparison of the mixture before and after the removal of the constituent by absorption in a suitable reagent is probably even more important than the comparison with a standard gas. In the previous paper the determination of ammonia and of carbon dioxide in the mixtures of hydrogen and nitrogen existing in a synthetic ammonia plant and the determination of carbon dioxide in air were described. Chlorine, hydrochloric acid, sulfur dioxide, acetylene, water vapor, and many other gases in mixtures of certain kinds appear to be equally subject to determination by this method.

Instead of removing a constituent of the mixture by absorption, we may subject it to any other process which will cause its removal or change its form of combination. The most important process of this kind is that of exposing the gas, preferably in the presence of a catalyst, to a sufficiently high temperature to cause reaction between different constituents of the mixture. For example, the total amount of atmospheric gases in a hydrogen-filled balloon may be determined by comparing the gas with pure hydrogen as a standard, as described above. The oxygen may be determined very accurately, independently of other impurities, by comparing the conductivities of the gas before and after passing through a combustion furnace in which the oxygen is removed by its reaction with hydrogen.

An interesting application of this method is the determination of methane in air by the simple process of comparing the conductivities of the mixture before and after passing over hot copper oxide. The methane is burned to carbon dioxide and water vapor. The gas is either dried or saturated with water vapor at the same temperature both before and after combustion. The net result of the combustion is therefore the replacement of one molecule of methane and two of oxygen by one molecule of carbon dioxide. Since carbon dioxide has only about half of the conductivity of methane, while oxygen and air are intermediate, this results in a very considerable lowering of the conductivity of the mixture. Some results actually obtained by this method of analysis are shown in Table II.

Table II—Automatic Determination of Methane in Air

Volumetric Analysis Per cent CH_4	Analysis by Thermal Conductivity Method	
	Uncorrected Reading of Instrument	Analysis from Calibration Curve
0.0	—0.03	—0.03
2.5	2.20	2.5
5.0	4.67	5.0
7.65	7.69	7.7

METHOD 3. ADDITION OF A GAS TO THE MIXTURE TO BE ANALYZED, FOLLOWED BY METHOD 2—While the methods already described are probably applicable to a majority of the gas analyses of industrial importance, there are certain important cases where they do not apply, and still others where a modification is desirable. Let us consider, for example, the determination of oxygen in flue gas. After the removal of carbon dioxide, an approximate determination of oxygen could, perhaps, be made by absorbing the oxygen in an appropriate reagent and comparing the conductivity of the gas before and after the absorption, as in the case of the determination of carbon dioxide. The result would be affected, however, by the presence of hydrogen, methane, water vapor, ammonia, oxides of nitrogen, any trace of unabsorbed carbon dioxide, and even carbon monoxide. The effect of these gases is serious only because the difference between the conductivities of oxygen and of nitrogen, which is the principal remaining constituent, is small. If, however, hydrogen were first mixed with the gas, say in equal volumes, the conductivity of the residual mixture of nitrogen and hydrogen would be several times that of the oxygen removed, and the determination of oxygen would be accurate in spite of small variations in the composition of the residue.

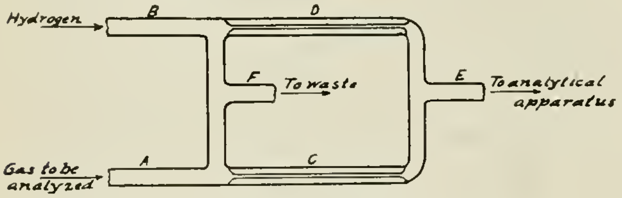

Fig. 1—Capillary Mixing Device

The essential feature of this method is the addition of gas in constant proportions to the mixture to be analyzed and the subsequent removal of the desired constituent. The device shown diagrammatically in Fig. 1 readily accomplishes the addition of a constant proportion of a gas. An excess of the mixture to be analyzed is passed through Tube A and an excess of the gas to be added, usually hydrogen, through Tube B. Part of each gas stream flows to waste through F and part flows through the connecting capillary Tube C or D to Tube E and thence to the gas-analysis apparatus. Since both ends of the capillaries are connected, the pressure drop through one is always the same as that through the other, and since the viscosity of a gas is practically independent of pressure and all gases have, within narrow limits, the same thermal coefficient of viscosity, it is only necessary to maintain the two capillaries at the same temperature in order to insure uniform mixing of the gases by this method. The relative proportions of the two gases may be readily varied by changing the relative lengths and diameters of the capillaries. Of course the relative proportions of the two gases will vary slightly with the composition of the mixture to be analyzed. The total measured effect of a change of composition is, therefore, to a certain small extent a function of viscosity as well as of thermal conductivity; but since viscosity and thermal conductivity are closely related functions of molecular motion, and since the relations depended upon in making a determination are entirely empirical, this fact makes no difference in the convenience or accuracy of the method.

The adjustment of the electrical instruments to give a direct reading on a linear scale is exactly the same as in the other cases. End resistances are determined by trials which make the slide-wire reading correspond to the percentage of the constituent sought in the mixture before the addition of a gas.

It is of interest to determine the amount of enriching gas which will produce a maximum reading by this method when the gas to be determined is removed and no other change takes place. For this purpose we may assume that the simple law of mixtures, as expressed by the following relation, holds:

If A, B, C, ... N represent the relative volumes of each constituent of a mixture, and a, b, c, ... n, the thermal conductivities of the respective gases when pure, the thermal conductivity of the mixture will be represented by the expression

$$\frac{aA + bB + cC + \dots nN}{A + B + C + \dots N}.$$

It is known that this simple law does not hold exactly, but it is, in most cases, a sufficiently close approximation to permit one to determine in advance the feasibility of using thermal conductivity methods for a definite purpose, and to choose between the several procedures usually possible.

Let A represent the number of parts by volume of the gas to be removed by absorption, B the number of parts of the residual gas in the original mixture, and C the number of parts of enriching gas to be added. Let a, b, and c represent the thermal conductivities of the three gases, respectively. It can be shown[1] by the usual method of differential calculus that the ratio of

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[1] If we represent by R the ratio of the conductivity of the mixture before to the conductivity of the mixture after the removal of the constituent of which the volume is represented by A, it is evident that the greatest sensitivity will be secured when dR/dA is a maximum. This condition is secured when

$$\frac{d^2R}{dA.dC} = 0 \qquad (1)$$

$$\text{Assuming that } R = \frac{\dfrac{bB + cC}{B + C}}{\dfrac{aA + bB + cC}{A + B + C}} \qquad (2)$$

the solution of Equation 1 involves the solution of an equation of the fifth power of C. It is evident, however, that for small values of A, the conditions which make dR/dA a maximum also make R a maximum. It has been found by experiment that R is not far from a linear function of A. Hence, for practical purposes we may always assume that the most favorable condition is found when R is a maximum.

Differentiating Equation 2 with respect to C, equating to zero, and solving for C leads to the equation given in the text.

the conductivity of the mixture after the removal of the desired constituent to the conductivity before the removal is a maximum when the amount of gas used for enrichment is in accordance with the following formula:

$$C = \frac{c(a-b)B \pm \sqrt{c^2(a-b)^2B^2 + (c^2-ac)(acAB + acB^2 - abAB - b^2B^2)}}{c^2 - ac}$$

The sign before the radical is positive when c is greater than a, and negative when c is less than a.

By substituting the appropriate values in this equation we find, for example, that the maximum reading for small variations of carbon dioxide in air is obtained when hydrogen is added in the ratio of 0.16 to 1. The maximum reading for small amounts of oxygen in nitrogen prepared from the air is obtained when hydrogen is mixed with the gas in the ratio of 0.44 to 1; the most favorable condition for determining variations in the percentage of oxygen in nearly normal air is obtained by adding hydrogen in the ratio of 0.39 to 1. Hydrogen could be determined in helium by adding carbon dioxide and passing over hot copper oxide. The most favorable condition would be obtained by adding 3 parts of carbon dioxide to one of the original mixture.

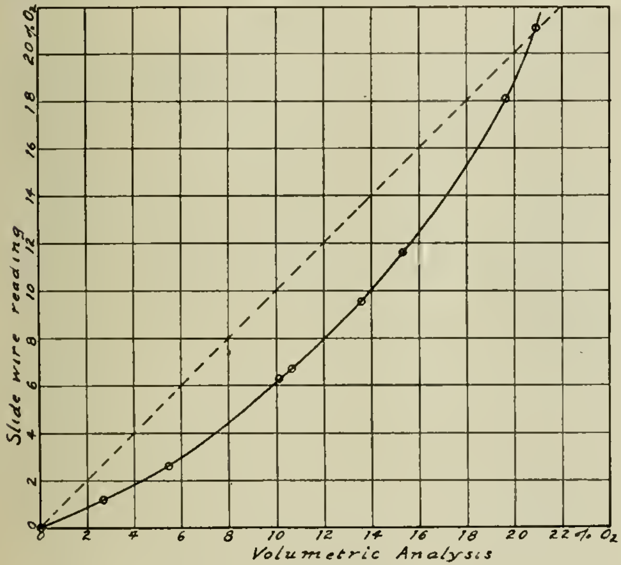

Fig. 2—Determination of Oxygen in Mixtures of Oxygen and Nitrogen

In the determination of methane in mixtures of nitrogen, methane, and helium, oxygen is added in constant proportions by means of capillaries, not for the purpose of altering the thermal conductivity of the mixture, but to permit the combustion of the methane. After the addition of oxygen, the determination of methane is made in the same manner as described above for the determination of methane in air. This method has been successfully used with a recorder. The end resistances were adjusted to make the slide-wire reading agree with the volumetric analyses of mixtures containing 0.0 and 9.8 per cent of methane. The recorder then indicated 4.75 per cent of methane in a mixture in which a volumetric analysis indicated 4.73 per cent of methane.

Fig. 2 shows graphically the results obtained by a procedure in which hydrogen is mixed with the gas for the double purpose of effecting a reaction and serving as an indicator of the extent of the reaction by modifying the conductivity of the residual gas. Here oxygen in mixtures of oxygen and atmospheric nitrogen was determined by mixing the gas with an excess of hydrogen by means of the capillary device, passing the mixture through a combustion tube, and comparing the conductivities of the mixtures existing before and after the combustion. The readings depend upon the amount of hydrogen left in the nitrogen after the combustion, and since there is a change of two volumes of hydrogen for every one of oxygen, the method is extremely sensitive. It will be observed that all the points fall very close to a regular curve, which happens to have several times as great a curvature, over a range of 20 per cent, as does the calibration curve for any other determination thus far made.

METHOD 4. SUCCESSIVE COMBUSTION WITH OXYGEN AND HYDROGEN—A difficult class of mixtures to deal with by comparisons of thermal conductivity is that of mixtures of various combustible gases containing hydrogen and, in some cases, oxygen. For the purpose of analyzing such mixtures, the following method has been applied successfully in the laboratory to the determination of carbon monoxide in the presence of large amounts of hydrogen.

Into a slow stream of the gas to be analyzed is run a stream of oxygen from an electrolytic generator having platinum electrodes and containing a potassium hydroxide solution as the electrolyte. The mixture is passed into a small electrically heated combustion tube, containing, preferably, copper oxide, and through a carbon dioxide absorber. It is then mixed with the hydrogen from the electrolytic generator supplying the oxygen and passed through a second combustion tube similar to the first. The electrolysis of an alkali (freed from carbonates by precipitation with barium hydroxide) between platinum electrodes produces hydrogen and oxygen in exactly equivalent proportions. Let us suppose that nitrogen or other inert gas were alone in the original sample. Then the hydrogen and oxygen introduced will combine in the second furnace to form water which may be eliminated, leaving the original gas unchanged. If, however, the original mixture contains carbon monoxide, methane, or other combustible constituent, an amount of oxygen sufficient to burn the combustible gas completely will be removed in the first combustion tube, and a corresponding amount of hydrogen will be in excess in the second. The gas leaving the second combustion tube will, therefore, contain hydrogen in place of all the combustible gases originally present. If, as is usually the case, the inert gas is of constant composition (atmospheric nitrogen), the oxygen equivalent of the total amount of combustible may be found directly and accurately by a comparison of the gas resulting from this so-called "double combustion" with a standard gas (hydrogen or air). Since the hydrogen in the original gas was replaced by hydrogen, a comparison of the gas before and after the double combustion process gives directly the sum of the combustible gases, *other than hydrogen*, present.

If it is the above data that are desired, oxygen, if originally present, must first be removed by bubbling through a solution of potassium pyrogallate or other reagent. However, if it were desired to learn the excess of reducing gases over the oxygen present, these data could be recorded directly by performing the double combustion as indicated and comparing the resulting mixture with a standard gas. The excess of combustible gas other than hydrogen over the oxygen present could equally well be recorded directly, in case anyone were interested in such data. A comparison of the mixtures resulting from the double combustion of two samples of the gas to be analyzed, from one of which the oxygen was first removed, would obviously give the oxygen content of the gas directly.

Table III gives results obtained by this method in the determination of carbon monoxide in a mixture of nitrogen and hydrogen. Unit A consisted of a thermal conductivity unit, having active wires of 1 mil (0.025 mm.) platinum 15 cm. long, and a Kohlrausch slide wire of approximately 30 ohms resistance. Unit B consisted of a thermal conductivity unit having active wires of 2 mil (0.05 mm.) platinum 10 cm. long, and a 7-ohm slide wire from a Leeds and Northrup recording Wheatstone bridge. The extension resistances of the slide wires had, of course, been adjusted previously to making the readings here given.

TABLE III—DETERMINATION OF CARBON MONOXIDE IN A MIXTURE OF NITROGEN, HYDROGEN, AND CARBON MONOXIDE

Volumetric Analysis			Analysis by Thermal Conductivity Method. Uncorrected Reading of Instrument	
			Unit A	Unit B
Per cent H_2	Per cent N_2	Per cent CO	Per cent CO	Per cent CO
66.1	33.7	0.21	0.21	..
69.4	29.5	1.10	1.12	..
70.5	27.4	2.13	2.13	..
70.3	27.4	2.25	2.25	..
70.0	27.2	2.77	2.77	..
68.8	26.6	4.62	4.63	..
68.7	26.6	4.70	4.70	..
51.8	5.8	42.43	42.43	42.4
51.0	5.6	43.43	43.53	43.5
50.2	5.6	44.15	44.24	44.5
48.5	5.4	46.25	46.20	46.1
47.4	5.2	47.40	47.40	47.4

COMBINATIONS OF THE BASIC METHODS—So many combinations of the basic methods already described are possible that it is not worth while trying to enumerate all of them. Probably the most important is the combination of methods in which a combustible gas containing carbon is burned and the resulting carbon dioxide is determined by absorption. This should prove a useful method, for example, in processes for the recovery of organic solvents. Oxygen may be added by means of the capillary device, if necessary, in order to secure complete combustion.

An equally interesting possibility is that of determining impurities in soluble gases, such as ammonia or carbon dioxide. The amount of gas in commercial ammonia, for example, would be so small as to affect the conductivity of the ammonia very slightly. If, however, we add a small amount of hydrogen to the ammonia by the capillary method and then absorb the ammonia, the amount of gas of low conductivity will be given with considerable accuracy by comparison with a standard gas according to Method 1. The residue so obtained would be in excellent condition for a determination of each of the individual absorbable constituents, such as carbon monoxide and oxygen, according to Method 2. If a second sample of ammonia were absorbed without the previous addition of hydrogen, and the residue compared with a standard gas, a comparison with the first sample would indicate the hydrogen with considerable accuracy.

This suggests again the possibility of obtaining useful data by comparing the thermal conductivities of the mixtures resulting from two different methods of treatment of the same gas. One example of this was mentioned in the case of the determination of oxygen in combustible gases of unknown composition.

Only one other example will be given, that of the complete analysis of the rather complex mixture existing in the gases which have passed through the reaction chamber in the synthetic ammonia processes. We are dealing here with a mixture containing approximately one part of nitrogen to three of hydrogen, some ammonia, argon, and considerable amounts of hydrocarbons, principally methane. It is important to know the amounts of both the hydrocarbons and the argon, since they become an increasingly large portion of the mixture as the gas is passed again and again through the ammonia converter, until they slow down the reaction to such an extent that it is no longer profitable to employ the mixture.

The mixture as a whole has a high conductivity, somewhat more than three-quarters that of hydrogen. The moderate amount of ammonia present can, therefore, be determined easily and accurately by Method 2, sulfuric acid being used as the absorbent. As compared with hydrogen, the conductivities of all the remaining gases lie close together, that of methane and of argon being on opposite sides of nitrogen. Hydrogen can, therefore, be quite accurately determined by a comparison with pure hydrogen, according to Method 1. Methane could now be most accurately determined by Method 4, but the apparatus would be quite complicated, and for the purpose in view, a simpler method will give sufficiently accurate results. Oxygen is mixed with the gas in slight excess (Method 3), the mixture is passed through a combustion tube (Method *2b*) and the resulting carbon dioxide determined by absorption (Method *2a*). The excess oxygen is absorbed, and the residual gas, containing only nitrogen and argon, is compared with air as a standard (Method 1). We thus have a direct determination of ammonia, hydrogen, and total carbon, and a determination of the ratio of argon to nitrogen in the residue after the removal of the other constituents.

GENERAL APPLICABILITY OF THE METHODS DESCRIBED

It is quite evident that the thermal conductivity method gives no information regarding the qualitative composition of an unknown mixture of gases; and that it can be applied quantitatively only when much is known about the probable identity and amounts of the constituents likely to occur in the gas mixture for analysis. The greatest usefulness of the method is certain to be in the continuous or frequent analysis of gas mixtures in industrial control work; and, fortunately, most mixtures of which it is industrially important to know the composition vary in a somewhat regular manner. Each class of gas mixtures must be studied individually with regard to the probable limits of variation of every constituent; but unless the mixtures are extremely complex a method can generally be found for indicating the composition of the mixture, although the data may not be expressed in the familiar units of percentage of the original mixture. Thus when several constituents are determined in a single mixture, the amount of some of them must generally be expressed in percentage of the residue remaining after the removal of other constituents. The data obtainable should not be less useful to a plant operator on that account after he has learned to interpret them.

SUMMARY

The limitations and advantages of the method of gas analysis depending upon thermal conductivity, which was described in an earlier paper, are discussed.

Several novel expedients are described by the use of which the method may be employed for the analysis of a great variety of gas mixtures of industrial importance, and their specific application is shown by many examples.

LABORATORY CONTROL OF WHEAT FLOUR MILLING[1]

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This article does not aim to present much information which might be called original in the strictly scientific sense. Its purpose is rather to point out an analytical procedure for the cereal chemist, particularly the flour-mill chemist, that differs considerably from those he ordinarily follows. This procedure is modeled after those used in control laboratories of industrial plants like smelters, sugar-beet factories, and others, where the process is one of refining or extracting the desired product from crude sources. In the laboratories of such plants samples of raw materials and of the different finished products are analyzed, thus keeping a check on the efficiency of factory operations. The flour-mill chemist ordinarily confines his activities to tests on the finished flour, but would increase the value of his services appreciably by including determinations of the flour content of wheat as it is received at the mill, and of the offal as it comes from the bins. From the results of such analyses the efficiency of milling operations may always be known. These results may also have other applications, as will be pointed out later.

THE WHEAT KERNEL

For milling purposes the wheat kernel may be regarded as composed of three distinct parts: the bran or outer seed coats, including the aleurone layer, the embryo or germ, and the inner endosperm or flour-producing portion. These different parts can be seen by cutting the kernel transversely or longitudinally. It is more difficult to determine what percentage of the whole kernel each constitutes. This can be done only by a slow and todious process of mechanical separation which Aimé Girard[1] performed as follows:

The kernels were soaked in water until they became plastic but not too soft, a treatment which required several days. Experiment showed that only an inconsiderable amount of material dissolved in the water in this process. The several layers of the seed coat were next removed by means of a scalpel, dried at 105° to 110° C., and weighed. The dry seed was split along the groove, and the germ was removed with pincers. Girard found the composition of the kernel to be

	Per cent
Bran (outer seed coats)	14.36
Germ	1.43
Endosperm	84.21
Total	100.00

Fleurent[2] reports the composition of three different wheats as follows:

	Average Wt. of Kernels Gram	Endosperm Per cent	Embryo Per cent	Bran Per cent
Russian	0.030	84.95	2.00	13.05
Algerian	0.048	84.99	1.50	13.51
Canadian	0.037	84.94	2.05	13.01

BRAN—The bran functions as an exo-skeleton or protective structure for the rest of the kernel, and is adapted to this purpose in chemical composition and physical structure.

Histological examination of cross-sections of the wheat kernel shows that the bran coat consists of several layers and membranes. The first three outer layers, called the epicarp, mesocarp, and endocarp, together constitute the pericarp. Beneath the endocarp are found, in the order named, the seminal tissue, the hyaline band, and the protein or aleurone layer. Botanically, the aleurone layer belongs to the endosperm, and is sometimes called the outer endosperm, but in commercial milling processes it is always separated with the bran, to which it adheres very firmly, and it may, therefore, be regarded as one of the seed coats of which the bran is composed.

The table of Girard (Table I) gives quantitatively the location of the different substances that are found in the outer covering, expressed in per cent of the entire bran coat.

Table I

Pericarp		
Water	3.58	
Non-nitrogenous fiber	24.43	
Nitrogenous material	2.41	
Ash	0.58	31.00
Seminal Tissue		
Water	0.92	
Non-nitrogenous material	5.06	
Nitrogenous material	1.25	
Ash	0.46	7.69
Hyaline Band and Protein Layer		
Water	7.23	
Cellulose material	29.61	
Nitrogenous material	15.21	
Fatty material	5.60	
Ash	3.66	61.31
Total		100.00

By adding the percentages of each substance as given separately for the three different regions in the preceding table, Girard computed the composition of the entire bran as follows:

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[1] The authors desire to express their thanks to Dr. I. K. Phelps for his helpful suggestions in this work and for his criticisms in the preparation of the manuscript.

[1] "Le Froment et Sa Mouture," **1903**, pp. 28–44.

[2] *Compt. rend.*, **124** (1896), 327.

Water	11.73
Cellulose material	59.10
Nitrogenous material	18.87
Fat	5.60
Ash	4.70
Total	100.00

Girard found 17.6 per cent of the bran to be water-soluble. Very dilute hydrochloric acid extracted 43.60 per cent more, 5.75 per cent of which was nitrogenous material, 33.5 per cent cellulose, and 4.35 per cent mineral matter. Treatment of the remainder with alkali removed 10.6 per cent, consisting mostly of nitrogenous matter.

THE GERM—The germ is the center of all physiological activity in the kernel. It consists of an embryonic plant with a cluster of leaves above and a radicle or embryo root below. On the side next to the endosperm is the scutellum, the connecting organ between the germ and the endosperm. The germ and scutellum contain active ferments and enzymes whose function it is to convert the reserve material of the endosperm into soluble matter, to be assimilated by the germ in the process of germination. The cells of the germ contain nitrogenous substances mixed with fatty matter, in the midst of which is the nucleus. All this material is soft and easy to modify as compared with the resistant substances in the other parts of the kernel. It is a well-known fact that mill products containing appreciable quantities of germ substance undergo decomposition more readily than do those which are relatively free from germ. This is probably due to the enzymes of the scutellum and to the sensitive nature of the germ proper. Table II gives the composition of the germ as found by Girard:

TABLE II

Water		11.55
Insoluble		
Fatty material	12.50	
Nitrogenous material	19.32	
Cellulose	9.61	
Mineral matter	0.80	42.23
Soluble		
Nitrogenous matter	19.75	
Non-nitrogenous matter	22.15	
Mineral matter	4.50	46.40
Total		100.18

THE INNER ENDOSPERM—The inner endosperm consists of inert material destined to serve as a food supply for the young plant in the process of germination. Its chemical constitution corresponds very closely to that of the purified and uncontaminated first middlings, which is practically pure endosperm. A histological study of the inner endosperm shows that it is made up of large cells with transparent walls, filled with a compact mass of gluten, in the midst of which are granules of starchy material. The parts nearest the aleurone layer are richest in gluten. According to Fleurent gluten consists of gliadin, glutenin, and very small quantities of congluten. The gluten at the pericarp contains more glutenin and less gliadin than that at the center. The quality of a flour for bread-baking purposes depends largely on the ratio of gliadin to glutenin in its gluten. Much research has been done to ascertain the optimum ratio but no definite conclusions have as yet been reached.[1]

MILL CONTROL

The object of commercial milling processes is to separate the three anatomical parts of the wheat berry as well as to reduce them to the desired granulation. Although it must be realized that proper and uniform reduction is essential, the efficiency of milling operations depends much more upon the completeness and the exactness of this separation than on the grinding or reduction. The function of the milling chemist, in addition to those already suggested, should be to trace the extent of the separation through its successive stages. On special occasions he may be of great assistance to the miller by making exact chemical measurements of endosperm (or flour) and offal (or bran) content of mill stocks before and after adjustments have been made on any particular machines. The endosperm, germ, and bran are composite substances which do not lend themselves to measurements by direct chemical methods, but a knowledge of their content in any stock may be obtained through a quantitative determination of some compound which is characteristically associated with these different parts of the wheat berry.

Table III, compiled from analyses made in the Food Control Laboratory on the best obtainable commercial products, shows approximately the chemical composition of the different parts of the wheat kernel in terms of those constants which are most commonly determined on mill products in a control laboratory.

TABLE III

	First Middling Flour (Endosperm)	Commercial Bran	Commercial Germ
Ash	0.368	6.45	4.47
Protein	12.08	16.49	29.89
Cold water extract	4.61	11.84	...
Acidity	0.08	0.65	...
Fat	0.75	3.58	10.02
Pentosan	2.25	22.72	5.38
Sugars	...	...	12.82
Starch	68.78	9.07	7.30
Moisture	12.08	13.00	13.00

A study of this table will show that the three different parts of the kernel have their characteristic constituents. Starch constitutes about 70 per cent of the inner endosperm and does not exist in either of the other parts, as may be demonstrated by a microscopic examination of pure bran coats or pure germ. The starch content of the samples of commercial bran and germ must, therefore, be regarded as due to endospermic contamination, and indicates imperfect separation in the milling process.

Pentosan may be considered the characteristic constituent of the bran, since its percentage is higher than that of the other bran constituents, while in the other parts its content is low. The figures in Table III represent the pentosan content of commercial mill products which are contaminated one with another. It is quite probable that most of the pentosan content in the sample of commercial germ is due to the presence of bran tissue, and that practically all of the pentosans in the offal come from this source.

Fat or ether extract is the characteristic constituent of the germ and aleurone layer. The following experiments were made in order to ascertain in a general way the distribution and location of fat in the wheat kernel. Kernels of different types of wheat were cut in two transversely, and the ends containing the germ were kept separate from the other ends. Fat determinations or ether extractions were made on the separate head and germ ends and also on the entire wheat. The results of these analyses, given in Table IV, indicate that the greater portion of the fat is associated with the germ. With the aid of facts which have already been brought out in Tables I, II, and III, further conclusions can be reached regarding the distribution and location of fat in the whole kernel. The fat content of the various parts as given in these tables are assembled in the following table:

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[1] Harry Snyder, Minnesota Station, *Bulletin* **54**, 42; *Ibid.*, **63**; Fleurent, *Compt. rend.*, **126** (1898), 1374; **123** (1896), 755; F. B. Guthrie, *Agr. Gazette, N. S. Wales*, **7** (1896), 583; H. A. Guess, *J. Am. Chem. Soc.*, **22** (1900), 263.

Table IV—Distribution of Ether Extract in Wheat

Description	Percentage of Ether Extract in Entire Wheat	Percentage of Ether Extract in Head Ends	Percentage of Ether Extract in Germ Ends	Percentage of Kernel Represented by Germ End	Per cent of Total Fat Contained in Germ End
No. 1 Hard R. Sp. Marquis..	2.32	0.91	5.34	31.8	73.4
Red Russ. West. Soft Winter.	1.90	0.96	5.22	22.1	60.7
Blue Stem Western White...	1.80	0.79	4.05	32.0	72.0
Durum from N. D..........	2.44	0.99	8.98	18.1	66.6

	Per cent
Pericarp	0.0
Seminal tissue	0.0
Hyaline band + aleurone layer	5.6
Germ	12.5
Inner endosperm	0.75

From these figures and those on page 899 giving the composition of the kernel, the percentage of the entire kernel, which the fat from each part constitutes, and the percentage of the total fat contained in each part may be calculated:

Source of Fat	Per cent of Kernel	Per cent of Fat
Bran, including aleurone layer	0.804	49.8
Germ	0.1788	11.08
Inner endosperm	0.631	39.1
Total	1.6138	99.98

These figures show that about three-fifths of the fat is concentrated in the hyaline band, aleurone layer, and germ, which constitute only about 10.3 per cent of the kernel. These parts belong to the offal. The inner endosperm constitutes the only true flour-producing portion of the wheat kernel; hence, ideally pure flour will contain no more fat than does the inner endosperm. This ideal condition is, perhaps, more nearly approached in the modern roller process than in the old burrstone process, where translocation of fat might more readily take place as a result of pressure and subsequent diffusion. A greater fat content in any mill stream must, therefore, be regarded as evidence of the presence of offal.

As has been stated previously, the germ and the scutellum contain a large number of enzymes, oils, and other compounds of great chemical activity, which seem to be intimately associated with the rapid decomposition of flour containing germ matter. The Food Administration realized the importance of this fact by allowing millers to remove as much as 5 per cent of low-grade stock from "war flour" to insure as complete a removal of germ substance as possible. Even during the period of flour shortage the improved keeping qualities of the remaining 95 per cent more than compensated for the sacrifice of this fraction. In view of these facts, every miller who wants to be assured of the keeping qualities of his flour should take special precautions to keep its germ content as low as possible. In order to know whether his precautions are effective, he should make fat determinations in the finished product. Starch, pentosan, and fat determinations in wheat and in mill products may thus be used as measures of the inner endosperm, bran, and germ content, respectively, of these products.

EXAMINATION OF COMMERCIAL MILL PRODUCTS

The procedure outlined in the preceding paragraph has been tested in commercial products, samples of which were sent to the Food Control Laboratory by the mills that produced them. They consisted of the cleaned wheat, and the flour and offal into which it was milled. Statements concerning flour yields were also sent by the mills. Starch and pentosan determinations were made by official methods as given in Bureau of Chemistry *Bulletin* **107**, revised, the diastase method being used for starch. Moisture was determined by drying in a vacuum oven to a constant weight, which required about 6 hrs. The results of these determinations, together with certain ratios and other calculated values, are assembled in Table V. Each group consists of a sample of cleaned and scoured wheat, and the flour and offal into which it was milled.

Table V—Chemical and Calculated Constants of Commercial Mill Products

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Wheat....	7.30	58.81	...	..	..	...	83.6	28.2	..
Offal......	20.78	19.66	23.1	..	..	...	27.9	27.6	..
Flour.....	3.19	70.42	76.5	76.6	77.2	1.42	..	..	91.5
Wheat....	7.81	53.71	...	..	..	...	81.7	29.0	..
Offal......	20.48	18.63	24.9	..	..	...	28.3	27.4	..
Flour.....	3.07	65.71	75.1	72.8	74.6	1.52	..	..	91.9
Wheat....	8.19	50.20	...	..	..	...	79.3	27.3	..
Offal......	19.06	23.41	30.91	..	..	...	37.0	28.4	..
Flour.....	3.20	63.28	69.14	72.3	68.5	1.58	..	..	87.2
Wheat....	7.35	55.40	...	..	..	...	83.0	27.4	..
Offal......	29.91	19.35	25.8	..	..	...	28.9	28.1	..
Flour.....	3.24	66.80	74.2	76.8	76.0	1.496	..	..	89.4
Wheat....	7.59	57.40	...	..	..	...	84.5	31.9	..
Offal......	21.30	21.00	25.8	..	..	...	30.9	29.5	..
Flour.....	3.12	67.90	74.2	75.5	77.6	1.473	..	..	87.8
Wheat....	7.54	54.30	...	..	..	...	82.9	29.8	..
Offal......	20.82	19.10	25.7	..	..	...	29.1	28.2	..
Flour.....	2.95	65.50	74.3	74.3	75.8	1.526	..	..	89.6

(1) Pentosan content on 13 per cent moisture basis
(2) Starch content on 13 per cent moisture basis
(3) Yield of flour and offal as reported by the mill, expressed in per cent of the wheat
(4) Yield as calculated from the pentosan content
(5) Yield as calculated from the starch content
(6) Flour conversion factor
(7) Flour content of wheat and offal calculated on starch content by use of conversion factor
(8) Pentosan content of flour-free products
(9) Milling efficiency

Formula 1:

$$\text{Flour yield} = \frac{(\text{Starch in wheat} - \text{Starch in offal}) \times 100}{\text{Starch in flour} - \text{Starch in offal}}$$

Formula 2:

$$\text{Pentosan content of flour-free wheat} = \frac{\text{Pentosan in wheat} - (\text{Flour in wheat} \times \text{Pentosan in flour}) \times 100}{100 - \text{Flour in wheat}}$$

Example:

$$\frac{7.30 - (83.6 \times 3.19) \times 100}{100 - 83.6} = 28.4 \text{ per cent}$$

CHECKING THE MILLER'S YIELD REPORT

The figures in Columns 4 and 5 may be used as a means of checking the yield report of the miller. These columns give the yields of flour as calculated from the pentosan and starch contents, respectively, by the use of Formula 1, which may be derived algebraically as follows:

	Per cent Starch
Wheat	58.81
Offal	19.66
Flour	70.42

Let x = flour in wheat
Then $1 - x$ = offal in wheat

$$70.42x + 19.66\,(1 - x) = 58.81$$
$$70.42x + 19.66 - 19.66x = 58.81$$
$$(70.42 - 19.66)x = 58.81 - 19.66$$
$$100x = \frac{(58.81 - 19.66)}{70.42 - 19.66} = 77.2 \text{ per cent}$$

Column 3 gives the flour and offal yield of the wheat as reported by the miller. The figures of Columns 3, 4, and 5 should, therefore, agree. Where they are not concordant, this is probably due to changes in moisture content and to difficulty in obtaining strictly uniform samples. The latter is particularly true of the offal. Furthermore, a faulty technique was exercised in sampling the offal without preliminary grinding. It is very difficult to obtain a truly representative one-gram sample of a material like offal as it comes from the mill. Grinding to a consistency nearly as fine as flour should be regarded as one of the essential steps preliminary to its analysis.

METHODS OF DETERMINING THE FLOUR CONTENT OF WHEAT AND FLOUR MILL PRODUCTS

EXPERIMENTAL MILL—The experimental mill has come into extensive use for the purpose of determining the flour yield of wheat, a result which is also interpreted by some millers as the flour content. The method necessitates expensive equipment and thorough skill in its use, and even with these assets the results obtained are usually inaccurate and otherwise unsatisfactory. A wheat will not necessarily yield the same amount of flour when milled in an experimental mill as when milled on a commercial scale. The ordinary experimental mill will not make as complete an extraction, and the yield obtained can in no way be regarded as the flour content of the wheat. It is particularly difficult to obtain comparable results with a mechanical process of this kind, since slight variations in equipment and technique affect its results very materially.

CHEMICAL METHOD—It seems quite possible that a chemical method of determining the flour content of wheat will overcome most of the objections inherent in the experimental mill. In this method the starch contents of the wheat and of the flour it produces are used as a basis for estimating the flour content of the wheat or of any of its mill products. A sample of first middlings flour from the wheat to be tested is first obtained by milling a portion in an experimental mill far enough to bolt out the first middlings, or from the regular mill run. This stream rather than the finished flour is selected because it represents more nearly the pure and uncontaminated inner endosperm. The starch contents of this stream and of the wheat are determined, preferably by the diastase method.

The starch conversion factor given in Column 6 of Table V is obtained from the equation

$$\text{Conversion factor} = \frac{100}{\text{Per cent starch in flour stream}}.$$

The starch content of wheat multiplied by this factor gives the flour content of the wheat. In case the flour content of a wheat is determined by the use of a factor obtained from the starch content of a commercial grade of flour, the result will be increased according to the amount of offal that was present in that commercial flour, and will show how much flour of that particular composition the wheat contains.

Under certain conditions it may be advantageous to use this method in conjunction with the experimental mill. For instance, a knowledge of the milling qualities of a wheat may be desired. These may be determined by the experimental mill, and the flour content of the resulting offal may be determined by the chemical method. Then the flour yield as obtained by the mill plus the flour content of the offal will give the flour content of the wheat. A chemist who has acquired familiarity with this method may at times dispense with the starch determination in the flour, and estimate with a fair degree of accuracy the flour content of a wheat from its starch content, by multiplying this value by an assumed or arbitrary conversion factor.

Results obtained by this method are expressed in Columns 6 and 7. Column 6 contains the flour conversion factors obtained from the starch content of the several straight flours. Column 7 expresses the flour content of the wheats and their offals. As the starch conversion factors which were used in the calculation of these results were obtained from the starch contents of straight flours, the values expressed in Column 7 denote not the true endosperm content of the several wheats, but the endosperm plus the offal content with which these straight flours are contaminated. This fact does not depreciate the value of these results, for they show the amount of flour of that particular composition, quality, or purity which the wheat is theoretically capable of yielding.

THE CONSTANCY OF PENTOSANS IN BRAN

Column 8 gives the pentosan content of the flour-free wheat and flour-free offal as calculated by Formula 2. The constancy of these figures is significant. Variations in the ratios of bran to germ in these different wheats and offals are probably responsible for variations in their pentosan content. The bran contains most, if not all, of the pentosans, whereas the germ contains little, or possibly none. Hence, a high ratio of bran to germ would cause a correspondingly high pentosan content. As this is so nearly constant it may be possible to use it as the basis for a practical method of approximating the offal content of wheat. The average of the values in Column 8 is 28.5, and the conversion factor calculated therefrom is 100/28.5 = 3.51. The difference between the pentosan content of wheat and that of its endosperm multiplied by this factor will give the offal content of the wheat. The pentosan content of pure inner endosperm is probably very constant. That of the several straight flours in Table IV is sufficiently so to warrant the use of their average, 3.13. The formula for calculating the offal content of wheat from its pentosan content will be:

$$\text{Offal} = (\text{Pentosan in wheat} - 3.13) \times 3.51$$
$$\text{Flour in wheat} = 100 - \text{offal in wheat}$$

Further work on this subject is now in progress.

MILL EFFICIENCY

The figures of Column 9 give the percentage efficiency of the several mills that furnished the samples.

These percentages are obtained by dividing the flour yields as reported by the mills by the flour contents of their wheats as expressed in Column 7, and multiplying the quotients by 100. Their efficiency is really lower than that indicated by the figures, which were calculated on the basis of the yield of flour which is appreciably contaminated with offal. The mills are given credit for this offal as though it were flour. This low efficiency is indicated in another way by the figures in Column 7 which express on a percentage basis the flour content of the several offals, which in one case runs as high as 37 per cent. The flour content of the offal in the first group, 27.9 per cent, is the lowest of all, and even in this case the loss is a serious one. This offal constituted 23.1 per cent of the wheat, according to the miller's own report. The flour in the offal, therefore, constituted 6.44 per cent of the wheat. The flour recovered by the miller was 76.5 per cent of the wheat. Out of every 100 lbs. of wheat containing 82.9 lbs. of flour, this miller recovered 76.5 lbs., and allowed the remaining 6.44 lbs. to go into the feed. Assuming that this flour sold for $12 a barrel and his feed for $60 a ton, he received $0.06 a pound for the flour and $0.03 a pound for the feed. The 6.44 lbs. which went into the feed brought him $0.193, whereas it should have brought him $0.386 if recovered as flour and sold as such. He lost, thereby, $0.193 for every 100 lbs. of wheat milled. In the case of a 1000-bbl. mill this loss would approximate $500 a day. Where the offal contained 37 per cent of flour the loss in a mill of the same size would amount to $900 a day. These figures bring out in an emphatic manner the prevailing low efficiency of modern flour mills. A knowledge of this condition should stimulate efforts among millers to make a more complete recovery of flour.

SUMMARY

1—The inner endosperm or true flour-producing portion of the wheat kernel contains all the starch and only very small percentages of pentosans and fats.

2—The bran tissue including the aleurone layer contains a high percentage of pentosans, 5 or 6 per cent of fat, and no starch. The pentosan content of the offal tissue is fairly constant.

3—The embryo or germ and the aleurone layer contain a high percentage of fat, and no starch.

4—The amount of fat and pentosans in any grade of flour is a measure of the amount of offal (germ and bran) contained in that flour. The amount of starch contained in wheat or any mill product is a measure of the amount of inner endosperm and, therefore, of the amount of flour contained in that product.

5—The accuracy of the flour-yield determination of wheat as made by the ordinary experimental mill is dependent on two very important factors: the skill of the operator, and the completeness of the equipment. The methods outlined in this paper will not be subject to the errors inherent in a milling test and will constitute a more accurate means of estimating the exact flour content of any given wheat.

6—The determinations of pentosans or starch may be used as a control of the miller's yield reports.

7—These determinations and formulas may also be used for obtaining the milling efficiency on a percentage basis.

WELDING THERMOCOUPLES IN THE ELECTRIC ARC

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The oxyacetylene flame usually employed for welding thermocouples is not always available, and with other gases it is difficult to secure the necessary heat without oxidizing the wires.

Base-metal thermocouples are easily and quickly welded in the electric arc, providing oxidation is prevented. A generous stream of illuminating gas is directed against the electric arc, and the twisted ends of the thermocouple wires are brought into the arc and fused together. Cooling for a few seconds in the gas prevents any trace of oxidation and no flux is required. Fifteen amperes alternating current has usually been employed, but for the larger sizes of wire a higher amperage is needed. The direct current arc is more efficient. The eyes of the operator must be protected by colored glasses.

THE WATER SUPPLY OF THE AMERICAN EXPEDITIONARY FORCES[1]

By Edward Bartow

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In the United States during the World War the construction and maintenance of water supplies for the Army was the duty of the Construction Division of the Quartermaster Corps; in the American Expeditionary Forces it was the duty of the Water Supply Service of the Engineer Corps. A regiment of water supply engineers, the 26th Engineers, was provided in the tables of organization of the A. E. F. This regiment was organized in the United States early in 1917, two of the companies were sent to France late in 1917, and the remainder in 1918. The Medical Department was to have control of the quality of water furnished, and detailed to each of the six companies of the 26th Engineers an officer of the Sanitary Corps and three men of the Medical Corps who should make water analyses under orders of the engineers. The Medical Department also detailed one Sanitary Corps officer to be sanitary inspector of water with each army division, under the orders of the chief sanitary officer of each division. Some of the officers of the Engineering and Medical Departments who were especially concerned with the quality of water felt that the division of authority indicated by these arrangements was unsatisfactory. To overcome the difficulty[1] the engineers were made responsible for the character of water delivered at the water points, and the Medical Department for any further treatment required. To carry out the requirements of the general orders, the Water Analysis Laboratories of the A. E. F. were established.

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[1] Published by permission of the Surgeon General, U. S. Army.

Fig. 1—Laboratory at Le Mans

In order to get the laboratories into operation as quickly as possible, officers and men qualified for laboratory and inspection work in water quality control were obtained as far as possible from troops in France, and requests were sent by cable through the office of the Chief Surgeon and General Headquarters for additional personnel.

LOCATION AND FUNCTION OF LABORATORIES

The personnel had direct charge from fixed laboratories over the quality of water in the Service of Supplies, including the base, intermediate, and advance sections, and from mobile laboratories accompanying the 26th Engineers, over the quality of water in the zone of the Army or fighting area. The personnel attached to the water analysis laboratories worked in coöperation with the division sanitary inspectors of water, who moved from place to place with their respective divisions.

Owing to the relation between the officer-in-charge of the water analysis laboratories and the French government, it was desirable that the central laboratory be located at Paris. The laboratories at Dijon and Tours were next in importance. At Dijon the laboratory was in the central laboratory of the Medical Department. At Tours it was near the office of the Water Supply Service of the Division of Construction and Forestry. Other laboratories were located at St. Nazaire (Base Section No. 1), Bordeaux (Base Section No. 2), Winchester, England (Base Section No. 3), Le Havre (Base Section No. 4), Brest (Base Section No. 5), La Rochelle (Base Section No. 7), Nevers (Intermediate Section, East), Neufchateau (Army Laboratory No. 1), and Le Mans (American Embarkation Center).

Each laboratory had control of water supplies for troops on the transports at the base ports, and for troops who might be stationed in cities, camps, supply depots, or hospitals in that part of the country administered from the headquarters of the section in which they were located. It was expected that Army Laboratory No. 1 and the mobile laboratories with the 26th Engineers would make analyses of water furnished at the water points and also any analyses desired by the sanitary inspectors of water. The sanitary inspectors of water with the divisions, moving with the divisions, had as their especial duties the supervision of sterilization or disinfection of water furnished the troops, and it was not expected that they would have time to do analytical work.

ANALYTICAL METHODS

The methods of analysis of the American Public Health Association and the American Chemical Society, together with the bacteriological standard adopted for drinking water to be used on common carriers in interstate commerce, were taken as the basis of analysis and interpretation of results. A "Bulletin on Water Analysis Adapted for Use in the Water Analysis Laboratories of the A. E. F." was compiled and distributed. The bacteriological methods have been reported to the Society of American Bacteriologists. The sanitary chemical methods included tests for turbidity, color, odor, residue, alkalinity, chloride, nitrate nitrogen, nitrite nitrogen, oxygen consumed, and total hardness. Industrial water analysis included determinations of carbon dioxide, alkalinity, non-carbonate hardness, magnesium, chloride, sulfate, and iron. It was also necessary to make determinations of the quality of bleaching powder and to determine whether a treated water contained an excess of chlorine.

ACTIVITIES OF THE VARIOUS LABORATORIES

Active work was begun at the Paris laboratory in January 1918, when the engineers sent samples to the laboratory with a request that analyses be made and an opinion given concerning their suitability for use in boilers, and concerning methods of treatment if the waters were not suitable.

Fig. 2—Laboratory Equipment at Nevers

St. Nazaire—About the same time representatives of the laboratories were sent to St. Nazaire to make a survey of the salinity of the Loire River. The water in St. Nazaire was insufficient for the needs of the city and the American troops stationed there, and it became necessary to furnish an additional supply. A dam and reservoir were constructed, but after the completion of the dam there was no rain and the reservoir remained empty. Five hundred thousand gallons of water per day had to be carried by tank boat from a fresh water stream up the Loire River and pumped into the city mains. A dam was

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[1] General Orders **34** and **131**, and *Bulletin* **55**, General Headquarters, A. E. F., 1918.

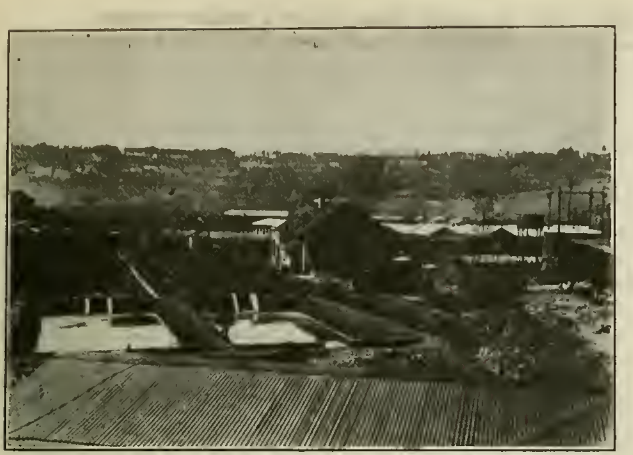

Fig. 3—Sludge Settling Basin at Langres

constructed on another river, the Brivet, to cut out the salt tide water and retain the fresh water. Before this dam was completed the water supply became so low that a portion of a fresh water transportation canal, the Trignac Canal, was cut off by a dam and used as a sedimentation basin. Alum was added as the water flowed through a weir in the dam, liquid chlorine was added to the coagulated and settled water, and it was then pumped to the St. Nazaire filter plant. The treatment was under the supervision of the St. Nazaire laboratory. The filter plant used by the French at St. Nazaire was of the slow sand type and barely adequate for the needs of the city. The Americans constructed a rapid mechanical filter of about 2,500,000-gal. capacity, and installed a liquid chlorine machine to sterilize the effluent. An additional filter plant was also constructed to supply water to the camp at Montoir, where freight from St. Nazaire was stored. The laboratory supervised both filter plants. Representatives from this laboratory visited regularly the hospitals and camps in Base Section No. 1, including artillery camps and four aviation camps.

BORDEAUX—At Bordeaux sufficient water was not available for the docks and the adjoining camps. After a study of geological conditions deep wells were drilled which at a depth of 800 ft. struck an excellent flow of splendid water. Each of three wells furnished 500,000 gal. a day. Daily analytical control of this supply was not necessary, but the laboratory had charge of several sterilizing machines which were connected with the supplies for Mt. Desert Hospital, the storage camp at St. Sulpice, where the freight landed at Bordeaux was stored, and at many other cities and camps in the base section, including several lumber camps. Representatives from this office also inspected water supplies in the leave area in southwestern France.

BREST—When Brest was chosen for a port of entry for American troops there was a supply of water sufficient only for the inhabitants of the city and for the French naval station located there. The water was obtained from gathering galleries located in the neighboring hills and flowed by gravity to the city and to the naval station. The barracks at Pontanesan were served by water from a spring which because of its doubtful quality had been filtered through trickling filters. With the influx of American troops none of these supplies were adequate, nor was there sufficient water to supply the transports, some of which could not carry enough for the round trip from the United States. A contract was made with the French naval authorities to allow water from as mall stream, Penfeld River, to pass into their mains to increase the supply, and an extension was made from the mains to the docks. Permission was given to use the water from the stream, provided it should be made of as good bacteriological quality as the water already in use, and also that it should have no taste and odor. In order to make the water available, a reservoir formerly used as a mill pond was enlarged and cleaned out by the American troops. Three hundred pounds of calcium hypochlorite were spread over the bottom, and water allowed to enter from the stream, forming a fairly concentrated solution. After this solution had remained in the pond for several hours it was replaced with fresh water from the stream. Liquid chlorine added to the effluent from the pond at the pumping station sterilized it.

Comparative tests made by the chemists and bacteriologists at the French naval station and by representatives of the Water Analysis Laboratories showed that the sterilization was satisfactory and that there was no taste or odor from an excess of chlorine, and the water was allowed to enter the mains. It later became necessary to build an additional reservoir of concrete and to construct an independent line to the Pontanesan barracks and the American pier. With the increased facilities, tank boats of 800-tons capacity could be quickly filled and the water transferred rapidly to the transports in the harbor.

On June 22, 1918, soon after the water from Penfeld River was put in use, a heavy rain following the most prolonged dry season in many years raised the water in the river. An intense amber color and a disagreeable taste developed. The alkalinity increased from 13 to 110. The chloride content which would naturally fall as the water rose showed a very small fluctuation, changing from 34 to 39. The bacteriological results were unsatisfactory, and use of the water was discontinued. Orders had been given to the officer-in-charge that if anything happened he should find the difficulty before the French laboratory discovered it, and the water had been shut off several hours before word came from the French laboratory that the water was unsatisfactory. The condition indicated special contamination, accompanying the increase in the quantity of water flowing into the river. The drainage area was carefully inspected and the trouble located in a branch of the stream, which had its source near a French aviation station where hydrogen for dirigible balloons was being made by the action of ferrosilicon on caustic soda. Arrangements were at once made with the French authorities to retain this waste matter in concrete basins, one of which was already completed in connection with a proposed plan for the recovery of soda from the waste product. From the concrete basins the waste would be used in soda recovery or hauled to the sea at a distance of about 8 kilometers.

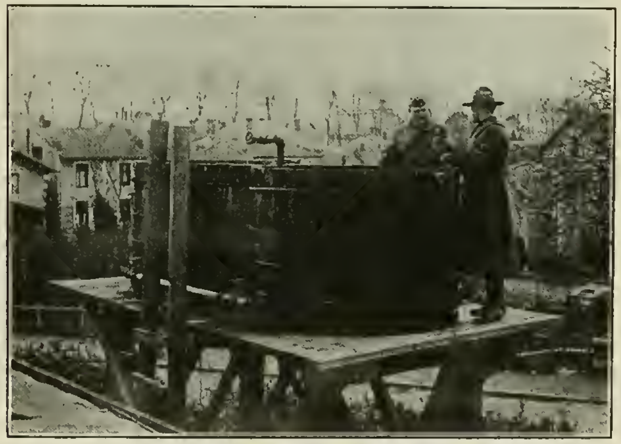

Fig. 4—Water Supplies for Troops in Transit at Sainte. Sterilization with Javelle Water

To prevent future trouble, as it was absolutely necessary to supply water for the allied shipping in the harbor, arrangements were made and material secured to treat the water in the upper part of the drainage area with alum to clarify and decolorize it, and to treat it farther down with sulfuric acid to neutralize the alkali. It was never necessary, however, to use these latter measures. The sterilization of the water with liquid chlorine was under the daily control of the laboratory, and it was of satisfactory quality for the transports and also for the camps at Pontanesan, which at times held as many as 80,000 men. The laboratory at Brest also had control of camps and hospitals in the base section.

LA ROCHELLE—La Rochelle obtained its water supply from gathering galleries dug in the low ground near the bay. The galleries were well protected by stone arches and under ordinary conditions the water was of good quality bacteriologically and of fair quality chemically. The mineral content was high, and during a dry season, because of the extra demand for water by the American troops, salt water from the bay seeped back, making the water so hard and salty that it could hardly be used for drinking purposes. The Americans made some improvement by sinking wells and digging additional ditches. It was necessary to use this hard water for boilers of locomotives and unloading cranes. The representatives of the Water Analysis Laboratories located at La Rochelle softened the water to be used in boilers, and recommendations were made for a water-softening plant. The softening of the water greatly increased the efficiency of the locomotives and cranes. This laboratory had quality control of several camps and hospitals in the neighborhood and was responsible for the use of javelle water, which is described later in this article.

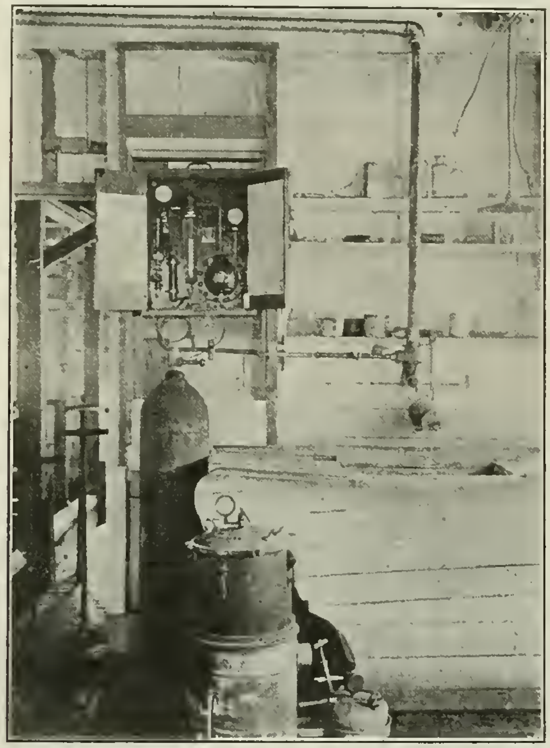

FIG. 5—WATER STERILIZATION WITH LIQUID CHLORINE

In order to take care of the sick and wounded several hospital centers were established in various parts of the A. E. F. These centers were planned to contain 20,000 beds, and in case of an emergency to handle an expansion to 40,000. The engineers constructed water systems for these units, and the purification and quality of the water was under the control of the Water Analysis Laboratories.

At Savenay, near St. Nazaire, a concrete dam 50 ft. high and 400 ft. across formed a reservoir of 140,000,000-gal. capacity. This water flowed by gravity to a filter plant where, after sterilization, it was pumped to an elevated tank and to the hospitals.

At Mars the water was obtained from a river which varied so in height that it was necessary to construct a deep pumping pit, heavily weighted to prevent floating, and with a water-tight wall several feet high above the surface to prevent flooding at times of high water. This construction is similar to that used on the Ohio and other American rivers which have a wide variation between high and low water.

At Beaune, Alleray, Langres, Mesves, and Bazoilles, installations more or less complicated were constructed by the American engineers. The quality of the water was under the control of the Laboratories.

WATER FOR TROOPS IN TRANSIT

Difficulty was experienced in obtaining sufficient water for troops in transit. The Railway Transportation Service, the Medical Department, the Engineer Department, and the Water Analysis Laboratories coöperated in an attempt to furnish water for filling canteens rapidly. At times of heavy troop movement, trains containing 1000 or more men would pass rapidly through the stations, giving but little time for the filling of canteens. Available water at the stations through which troop trains would pass was examined by the laboratories, and when it was found to be of good quality, a large number of faucets were installed by the engineers. When water was of doubtful quality, one or more tanks were erected, and a solution of bleaching powder added to the water in the tank. These tanks were connected with a suitable number of faucets in order that the troops might fill canteens promptly during their stay at the station. Pending the installation of tanks an attempt was made in several places to use lyster bags. These, however, were found unsatisfactory during rapid troop movements. They could not be filled quickly. It was necessary that the water should stand 30 min. after treatment, and trains would often pass at less than 30-min. intervals. For stations where the troops movements were small, lyster bags were fairly satisfactory.

WATER SUPPLY IN ARMY ZONE

In the army zone, water points were constructed by the engineers. Wherever possible wells were used, but in that part of the front line occupied by the Americans it was difficult to obtain sufficient water from wells. Filter plants were constructed to use water from streams. When entering an area where there was insufficient water or during an advance, the so-called sterilab was used. This consisted of a pump, filter, and sterilizing apparatus mounted on a truck. It could be sent forward with troops and as more permanent installations were installed would be relieved for service elsewhere. When clear water was available a combination of pump and sterilizing apparatus was sufficient. Stationary filter plants were often constructed and operated within the range of the enemy's shell fire. The drinking water was sterilized by liquid chlorine machines, by solutions of bleaching powder, or javelle water. More than 150 liquid chlorine machines were in use by the A. E. F., and were located from the base ports to the Rhine. Solutions of bleaching powder were used on a large scale at some places, but it was used most often in lyster bags. Tubes containing about one gram of calcium hypochlorite were added to 36 gal. of water in the lyster bag. The British used bulk calcium hypochlorite, after determining the amount to use by a test devised by Col. Horrocks. By the Horrocks test the amount of bleaching powder needed to furnish an excess of chlorine was determined, and the taste and odor due to a large excess were avoided. Attempts made by some of the American officers to determine the amounts necessary did not prove satisfactory, owing to variation in the amount of bleaching powder in the tubes. Javelle water was used to a large extent by the French. Automatic machines for the delivery of solutions in proportion to the amount of water pumped have been devised by Vila and Buena Varilla. The Americans used all of these methods, but sterilization in the lyster bag holding 36 gal. of water was especially characteristic of the American army.

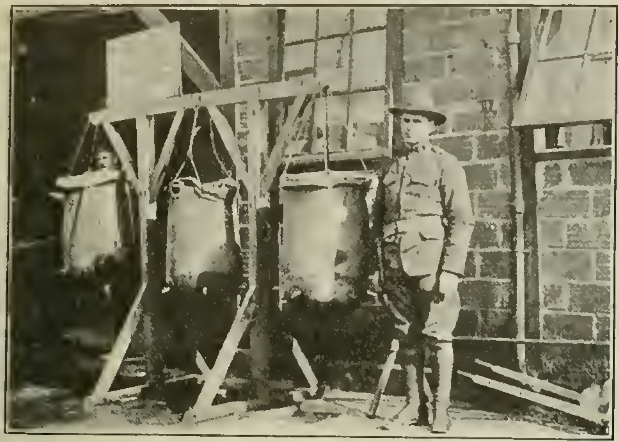

Fig. 6—Lyster Bags at Railway Station

A gram of calcium hypochlorite added to 36 gal. of water in the lyster bag was equivalent to treating the water with two parts per million of available chlorine. In the spring of 1918 it was noticed that there was a high percentage of defective tubes in the calcium hypochlorite furnished for use in the A. E. F. The laboratories at Bordeaux, Dijon, St. Nazaire, and Paris participated in studies of the quality and the physical condition of these tubes. The most extensive work was done at the Bordeaux laboratory. Some determinations of the actual weight of calcium hypochlorite and percentage of available chlorine were made, but, since a tube containing 0.3 of a gram of available chlorine was really desired, the percentage of chlorine in the salt was immaterial, provided the proper amount was present. Therefore, most of the analyses were made by titration of the contents of the tube without weighing it. By inspection alone, broken tubes, faultily sealed tubes, and tubes containing insufficient calcium hypochlorite could be discarded. If the tube was whole and the contents dry, the material would fall from one end of the tube to the other as a powder. The contents of such tubes were usually found to be of good quality. As illustrating the success of this method, from 720 tubes, 37 were picked out as supposedly defective. The available chlorine was determined in each of these, with the result that 100 per cent were found to have less than 0.2 g. of available chlorine. Fifty-three of the remaining supposedly good tubes were selected at random for analysis. Nine per cent of these tubes had less than 0.2 g., and 91.5 per cent had more than 0.25 g. of available chlorine. Beginning in the summer of 1918 all tubes coming into Base Section No. 2 by way of Bordeaux were inspected. Six and one-half per cent of the tubes of one lot were found defective, and 41 per cent of tubes from another manufacturer were found defective. As a result of this work suggestions were made through military channels that inspectors be placed in all factories manufacturing these tubes in order to eliminate to a certain extent the large number of broken and defective tubes received in France.

The Water Analysis Laboratories were called upon to analyze samples of alum offered to the engineering department for use in water treatment. Analysis was made according to the methods of the American Public Health Association and the American Chemical Society.

At the request of the air service, analyses of the mineral content of water from established aviation stations and from proposed sites for aviation stations throughout France were made. It was the purpose of the air service to soften the water with permutit for use in the radiators of water-cooled motors. Several equipments for water softening were installed in consultation with laboratories. The laboratories also had control of water treatment for several aviation stations.

At the request of the Quartermaster Department, water used at the laundry at St. Pierre du Corps was examined and recommendations made that a permutit water-softening plant be installed. The installation of this plant reduced the quantity of soap and sodium carbonate required, the washing was more easily done, and the washed materials, especially woolen goods, were in much better condition than when hard water was used.

As a result of examination of water at La Rochelle a lime-soda softening plant was recommended. This, however, was never constructed. Soda and a French boiler compound were used to treat the water added to the boilers.

IMPRESSIONS OF THE ITALIAN CHEMICAL INDUSTRY

Editor of the Journal of the Industrial and Engineering Chemistry:

Before leaving America I promised you to try to write a letter from each country in turn, regarding my impressions of the chemical industries therein. I have been so extremely busy that, although my experiences in England, France, and Belgium gave me some knowledge of the developments in each, I have been unable to put anything on paper. Now a day is at my disposal for rest here in this charming spot, and I have had such a wonderful reception as America's representative at the meeting here in Italy that part of it shall be spent in fulfilling my promise, so far as Italy is concerned. I am doubly urged to do so for the June issue of the Journal which you kindly sent is before me, with Mr. Hopkins' interesting article. While the statistical data upon which he bases his conclusions have led him to concede decided development to Italy's chemical industries, his conclusions fall far short of the reality, as you will note in what follows.

The second meeting of the International Union of Pure and Applied Chemistry, which brought me to Italy, was a grand success. Prof. Lormand, your French correspondent, has already, or will shortly send you a full account of it as a part of his July letter. I wish simply to add that the social functions were charmingly carried out, and were accompanied by an artistic coloring and delightful touch which I doubt if one ever finds quite so delicate as in this truly charming and "simpatica" country. The ladies for example will always remember the lovely individual bouquets that each found beside her plate at the banquet, nor will the memory be less lasting from the fact that each was tied not only with the colors of Italy but with the colors of the home country of the recipient.

Following and during the meeting, we were taken to see something of Italy's chemical development, and this is where you are specially interested. We were received with charming and openhanded hospitality, but best of all we were actually shown the plants and their details, not simply walked through them as is so often the case in America. The Italian was justly proud of the work of his chemists and engineers, and was anxious that his guests too see something of their actual accomplishments. There was no secrecy so far as we were concerned; they described their methods and their apparatus, and seemed to invite inquiries where anything was obscure. If I can judge from the treatment I received, one would believe that Italy's industries had reached that stage where full coöperation was deemed to be the policy best for all.

Naturally, Italy's plants, like many of our own, are being changed, for the main part, from the production of war material to uses consistent with peace. The plant at Segni, known as the Bombrini Parodi-Delfino, which was manufacturing balastite so successfully when I visited it first in 1916, is manufacturing sulfuric and nitric acids for the general chemical markets, and the nitroglycerin is now largely used for the manufacture of dynamite for commercial explosive. The plant owes its success chiefly to the energy and ability of the brothers Leopoldo and Sebastino Parodi-Delfino.

The "Electrochimica Pomilio" located in Naples, is a comparatively new venture of Ing. Prof. Umberto Pomilio, who was a genial and delightful host who could and did address his guests fluently in three languages, as well as entertain them royally. His plant is successfully turning out caustic soda, bleaching powder, liquid chlorine, hypochlorites, and other products arising directly and indirectly from the electrolysis of salt. The plant is noteworthy and almost unique in the fact that it does not use a pound of coal or other fuel, depending entirely on electricity for both its power and evaporation. The evaporation is done by compressing the steam of evaporation mechanically and using it over and over again, supplying the small necessary heat addition by a small Reavell boiler, run by electricity, which gives 800 kilos of steam per hour. From 1 kilowatt hour they get in practice 7 kilos of steam. The day spent at this plant and as the guests of Prof. Pomilio at Pompeii will always be remembered by those present.

A few days later we were all entertained by Ing. Ferdinando Quartieri, chief owner and manager of the largest chemical works in Italy, with branches at Cengio, Ferrania, Vado Ligure, Linate, Turin, and at Rho near Milan. These works for the main part were used for the manufacture of explosives and belong to the "Società Italiana Prodotti Esplodenti." They are now rapidly being converted to peace uses and are actively producing on a large scale. It was my privilege to visit the plants at Cengio, Ferrania, and Rho. Lack of time, only, prevented me from seeing the others. Mr. Quartieri, speaking at least three languages easily, and known personally to many of our American chemical manufacturers, was, like those already mentioned, a model host who left no stone unturned that his guests, both in his plant and in his home, might enjoy the full measure of his hospitality. At Cengio, at Ferrania, and at Rho many new and attractive buildings were being erected to meet the increased demand and to utilize the output of the old war plants. Coal from America and from England was being distilled, the coke and gas used or sold, and the by-products all recovered and used in the dye industry. Contact sulfuric acid plants and unusually well-designed nitric acid plants were still being utilized. Benzene, toluene, naphthalene, and their derivatives were being turned out in quantity. The saccharin plant was running full blast, and not simply aniline but many intermediates for the dye plant at Rho were being produced. Again at Ferrania, some fifteen miles away, a smokeless powder plant was now being converted to produce celluloid, photographic films, artificial leather, bakelite (here called sepilite), etc., and was even now actually turning out in quantity most of these products. At Rho a large dye plant was in active operation, already producing some 250 different dyes, many of them in large quantity. Its diazo dyes building was especially a model in design and arrangement. Its research laboratory was commodious, and contained many well equipped special laboratories, and, was easily comparable in its resources, equipment, and personnel with the research departments of our most advanced American corporations. The S. I. P. E. company now employs 92 chemists, most of them Ph.D's., and about half of them are in this plant at Rho. The plant is also well fitted with all kinds of sanitary arrangements, with baths and lockers, and with lunch rooms for the laborers. Its workmen seemed happy and contented, and it had suffered from no labor troubles. The success of this large corporation, now growing rapidly, seems to be centered around the personality of Ing. Ferdinando Quartieri, whose energy and vision is giving to Italy a dye industry which on first thought might seem impossible in a country so devoid of coal. Careful consideration will, however, show that inasmuch as Italy must have the products of coal, as she has comparatively cheap labor and an excellent outlet to the eastern markets, the cheapest way for her to obtain her coke, her gas, her toluene, her benzene, and the intermediates and finished products therefrom is to bring them to Italy in the original raw material, coal itself. Two other important new plants for dyes, the "Materia Colorante Bonelli" at Cesano-Maderno and the "Societá A. Bianchi" at Rho, are also well under way in dye production; the first is making a specialty of indigo, and the second is developing especially the vat dyes. I was invited by Director Prof. G. Poma to visit the former, he even offering to send his automobile here, some thirty miles, to get me, but important engagements in Switzerland unfortunately prevent me from accepting.

Also through the courtesy of one of our own A. C. S. members, Prof. Giuseppe Bruni, who is known personally, as well as by reputation, to many of our members, as he was present at the Congress of Applied Chemistry in New York in 1912, I was introduced to the Pirelli's, father and son, was taken through their immense factory, and entertained in their charming home. Pirelli & Company have large rubber goods and insulated cable factories not only in Italy, but also in Spain and in England. Their factory is being enlarged rapidly and is approaching in size, if indeed it does not already equal, some of those at Akron. As I had the pleasure of a visit recently to the Akron factories, it was especially interesting to find how vigorous and up-to-date was this great Italian industrial undertaking. Here, too, under Prof. Bruni's able leadership were to be found the modern research laboratory and the appreciation of research which is the sure sign of progress.

I leave Italy tomorrow with sincere regret, for I feel that I am beginning to understand her people. Four things stand out plainly from my observations.

First, Italian chemical plants are artistically built without much extra cost and with no loss in efficiency. They are clean, up-to-date, and attractive to the eye. In this particular they are greatly superior to anything I have seen in America.

Second, the Italian scientific and engineering chemist is, on the whole, equal in training, vision, energy, originality, and application to those of any country.

Third, Italy must have raw materials, especially coal, for the success of her chemical industry, and there is a real opportunity for Americans controlling these basic materials to enter with profit into some form of partnership arrangement with Italian firms.

Fourth, the Italian chemical industry is going to be successful, and must be reckoned with in the world's markets, especially in those countries lying to the east of Italy and reached via the Mediterranean Sea and by the Suez Canal.

I hope to follow this letter home in about three weeks, but must first go to Switzerland and into Germany.

With best wishes to all,

Cordially yours,

Charles L. Parsons

Hotel Villa d'Este
Cernobbio, Lake Como
July 2, 1920

ADDRESSES AND CONTRIBUTED ARTICLES

INDEXING REFERENCES

By Alfred Tingle

Analytical and Research Laboratory, The E. B. Eddy Co., Ltd., Hull, P. Q.

Received March 18, 1920

The problem of indexing references to current literature was found, till lately, particularly troublesome in the Customs and Inland Revenue Laboratory, where the scope of work done is unusually wide. The Customs Chemist may be called upon to analyze any material imported into the country; he must also be ready to say how the material is made, what are its uses, what other material it most nearly resembles, and to answer almost any other question which can reasonably or unreasonably be put to a chemist. On one occasion a package of rennet tablets was received with an official request for information as to whether this was genuine rennet, and if so whether it was made from the stomach of a cow, of a calf, or of a pig.

Since omniscience is expected of him, it behooves the Customs Chemist to have at his command either an exhaustive knowledge of the literature or a very lively imagination, while a combination of the two is preferable. The former requisite involves not only extensive reading and note-taking, but also a sound and simple system of filing notes.

The system now in use has proved so effective and elastic that it seems worth describing. Its adoption brought order out of a chaos of cards. It should be noted that this system was suggested by, and is only an elaboration of, that described by Arthur Marshall.[1]

In the first place it is necessary to select from the library certain specific works as "index volumes." All these index volumes together must cover the field on which notes will be made. They must be carefully chosen to avoid overlapping as far as possible, while leaving as little as possible untouched. At the same time their number should be reasonably small. Profundity, and even accuracy, are less essential than comprehensiveness.

For each index volume a blue "Index Card" is used, having a "flag" along three-quarters of its upper edge. This flag bears the name of the index volume to which it corresponds. For each chapter or section of the index volume a "Sub-Index Card" of contrasting color (buff) is provided, its "flag," of half length only, being inscribed with a contraction for the name of the index volume and with the chapter number, section, or set of pages to which it is the key. The notes to be filed are made on ordinary ruled white cards of suitable size. In this laboratory 5 x 3 in. has been found most generally suitable.

An example will best illustrate the manner in which the filing system works. It has been found here that the organic field can be pretty adequately covered by the following index volumes: Allen's "Commercial Organic Analysis," 8 vols.; Martin's "Industrial and Manufacturing Chemistry (Organic)," 1 vol.; and Beilstein's "Handbuch," 4 vols. Supplementary volumes are not included as part of this index. The use of 13 blue cards is thus involved, each with its complement of buff cards to differentiate chapters. A certain paper is to be noted for future reference: a white card is therefore made out thus:

> Some Notes on Sandalwood, Its Assay, Yield of Oil, and Changes in the Oil during Distillation. By C. H. Briggs, *J. Ind. Eng. Chem.*, 8 (1916), 428; Abstr. in *J. Soc. Chem. Ind.*, 35 (1916), 706. Method of assay is given, with some results and the constants of certain samples of oil are noted. See original paper.

This may constitute the reference. For filing, such a card should be made out in triplicate.

Sandalwood oil is dealt with, so far as the index volumes are concerned, in Allen's "Organic Analysis," Vol. IV, p. 391 (*i. e.*, in the section paged from 303 to 461), in Beilstein, Vol. III, p. 549 (*i. e.*, in Section XII B), and very briefly in Martin's "Industrial Chemistry (Organic)," p. 137 (*i. e.*, in Section XIII).

The three reference cards will therefore be placed

(I) Under the blue Index Card "Allen, Vol. IV," and its buff Sub-Index Card "A IV 303–461."

(II) Under the blue Index Card "Beilstein III," and its buff Sub-Index Card "B III, XII B."

(III) Under the blue Index Card "Martin Organic," and its buff Sub-Index Card "M O XIII."

A less comprehensive paper would not require to be indexed under so many headings. For instance, had this paper been concerned only with an analytical method, a single card would have sufficed. It would have been placed under "Allen IV" and nothing would have been entered under "Martin" or "Beilstein."

As an example of how information thus filed may be found when required, it may be supposed that information is sought on the manufacture and assay of a disinfectant of the Lysol type. Such information as can be found in Lunge's "Coal Tar and Ammonia" or other standard works available having been assimilated, the "Index Volumes" are consulted. It is an easy matter to know which of these few books will contain anything pertinent; they are Allen's "Commercial Analysis," Vol. III, in the section paged from 287 to 390, and Martin's "Industrial Chemistry (Organic)," Section XII (where, however, the subject is hardly more than touched). We may therefore be sure that any references to the current literature on this subject which have been filed are to be found under the blue Index Card "Allen, Vol. III" and its buff Sub-Index Card "A III 287–390," or else under the blue Index Card "Martin O" and its buff Sub-Index Card "M O XII." References bearing on analysis may be more particularly expected in the first-mentioned place, while in the second will be those bearing on manufacturing methods. The search thus narrows itself to glancing over the headings of perhaps one or two dozen reference cards.

Every index-maker must select his own set of index volumes to meet his own requirements. Those mentioned above were found to serve fully the purpose of the Customs and Inland Revenue Laboratory in the field which they are used to cover.

CRITICISMS AND THEIR ANSWERS

The foregoing has been subject to certain criticism while in manuscript. The maximum of clearness will probably be attained by giving the criticism, following each of its points with the answer.

I—How would you handle such difficulties as might arise from the fact that sometimes in a reference book a given subject is treated in more than one chapter or part of the book? This would seem to be a confusing circumstance.

No more confusing than the reading of the book. A card is made for every section of every index volume which contains anything pertinent. The cards may be considered as footnotes, to be inserted wherever needed.

II—The importance of comprehensiveness in the selection of the so-called index volumes for a given field is emphasized. There would be a limit, of course, in one's ability to secure this desirable feature and some might wonder how a subject (possibly a new one since the publication of the index volumes) would be handled. The system would appear to have a limitation unless there were some supplementary method of taking care of new subjects.

Even the "newest" of subjects is related to something which has gone before. Had it been the writer's task to index by this system polonium and radium when they were new, he would have placed them (temporarily, of course) under uranium. The system does not profess to abolish the necessity for some consideration before placing cards in order.

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[1] *J. Soc Chem. Ind.*, **37** (1918), 360*r*.

III—The system is of course dependent on the indexes of the index volumes, which would very likely vary both in quality and in method. Usually the indexes of books do not contain cross-references. To a small extent, at least, the lack of a place in the system for cross references might be a handicap at times.

This seems to be founded on a misunderstanding. In practice the Table of Contents of the volumes is generally more important than the Index, since the Sub-Index Cards refer to sections of the volumes, not to individual pages. The writer sees no difficulty about cross-references: all that are desired can be introduced on the cards. It should be clearly understood that the cards must be made out and filed by a *chemist*—one of the men who will use them—not by an ill-educated clerk.

IV—The system seems to be really more a filing system than an indexing system, so that possibly it would be more appropriate for the title of the article to contain the word "filing" in place of the word "indexing."

According to the writer's vocabulary and English dictionary, it is both. The cards, having been filed, constitute an index.

V—I believe that the article would be of real interest to the individual or laboratory which desires to keep its own record of the literature and that the system might be very useful, particularly in laboratories of a certain type. There are a good many chemists who prefer to keep individual records of the literature. It has always seemed to me that it would be much simpler and just as satisfactory to depend upon the abstract journals, particularly since the very considerable amount of work involved in keeping an individual record up to date would be avoided.

Indexes to abstract journals, like Christmas, come but once a year, while it is often necessary to look for a reference only a few months old. Even the best of indexes is constructed on the basis of "Subject" and "Author" only, though "Subject" is usually translated "Title." There may be a very important subject dealt with in a paper yet not mentioned in the title and consequently not found in the journal indexes. Turning to one at random, the writer finds "Aluminum and Ferric Oxide" followed by a page reference. Truly illuminating.

WOOD ALCOHOL NO LONGER: HEREAFTER METHANOL[1]

By Charles Baskerville

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Wood (methyl) alcohol poisoning is an unique problem in that it involves not alone physiological changes and technical matters having to do with production and distribution of the toxic agent, but sociological factors as well.

The "adiophorous" spirit obtained by distilling wood (Boyle, 1661) was thought by Taylor (1812) to be a new kind of *ether;* in fact, he called it "pyroligneous aether." Dumas and Peligot (1835) established its resemblance to ethyl (*ether*) alcohol and named it methyl alcohol from the Greek *μέθυ* mead and ὕλη wood. In fact it may be recalled that the word *alcohol*, derived from the Arabic, *Al Kohl*, at one time meant a fine powder and only later meant spirits.

Commercially the destructive distillation of hard woods (refuse) is the main practical method followed for the production of methyl alcohol in America, although in Europe it has been obtained from peat and as a by-product from vinasse, and in the manufacture of wood pulp by a soluble sulfite process. The numerous synthetic methods known at present are too costly to be practiced on a commercial scale. The condensed tarry and acid products distilled from wood are subjected to partial purification by distillation. This crude material, about 80 per cent pure, is then usually shipped to centrally located refineries in tank cars, drums, or barrels for further purification and rectification.

This crude wood alcohol, "wood spirit," "wood naphtha," a vile-smelling, greenish yellow to dark brown, nauseous liquid, is a complex mixture containing a variety of impurities. They are removed in the main in the first refining, yielding a product containing about 95 per cent methyl hydroxide. In 1896 processes for greater refinement were put into operation, so that about 1906 a deodorized product (97 to nearly 100 per cent) was placed upon the market in the United States under such names as "Columbian Spirits," "Eagle Spirits," "Hastings Spirits," "Colonial Spirits," "Manhatten Spirits," "Union Spirits," and "Lion d'or;" in Canada as "greenwood spirits," and "standard wood spirits;" and in Germany in 1912 as "pro spirit." Technically it was called methyl hydrate, carbinol, methylic alcohol, methyl hydroxide, and methanol. The pure substance is a colorless, mobile liquid, having a pure vinous odor, similar to that of pure ethyl alcohol, and possesses a burning taste.

These facts of names and their meanings are not known by all technical men. They are even less known to the "man-of-the-street;" but the layman does know that "alcohol" is the stuff which makes drunk come; that it is the stuff that cheers when downhearted; that uncontrolled it has been a curse in the world; that it is the "real thing" in the disguise of beer or light wine, which formerly rested him when the arduous day's work was done. So when he sees the can or vessel with the label "alcohol" on it, and as he knows "alcohol" is the thing that gives the "kick," rest, or cheer, without considering the qualifying words "wood," "methyl," or what not, he is going to take it. He is little deterred by the "poison" label, for he has a more or less similar idea from the pictures of intemperance, and still he drank. Therefore, the term *alcohol* should cease its present significant use, at least in chemical literature. Technically, all alcohols should become known as "-ol" bodies or hydroxides, as "methanol," "ethanol," "propanol," "butanol," etc.; methyl hydroxide, ethyl hydroxide, propyl hydroxides, etc.

In 1906, after a vigorous campaign, the United States followed England, France, Germany, and other European countries by enacting laws permitting the general use of a tax-free domestic alcohol for industrial purposes, and for light, heat, and power.[1] This law has made us a self-contained nation in regard to certain medicinals; ether, ethyl chloride, chloral hydrate, nitrous ether, and numerous synthetics may be mentioned in illustration. To emasculate alcohol, as it were, the law requires that tax-free alcohol for use in the arts and industries shall have first mixed with it (under close supervision) substances which "destroy its character as a beverage or render it unfit for liquid medicinal purposes." On account of its poisonous properties, difficulty of removal from the resulting industrial alcohol, non-interference with many of the industrial purposes for which the denatured product was intended, and a desire to avoid the destruction of the methyl alcohol business, for methyl alcohol was cheap at that time, the first act designated it as a denaturant, and the Commissioner of Internal Revenue selected it as the principal one.

Up to date some forty-one formulas for "specially denatured alcohol," to be used for designated purposes only, have been authorized under the several acts. Five formulas for "completely denatured alcohol," which may be used for light, heat, and power, have been authorized. One of each of these has been revoked.

The control of the former class (special) is so complete, involving as it does the moral character of the users, that little danger attends its use. One formula (No. 30) allows the addition of as much as 10 per cent of the purest methyl hydroxide, but its use is restricted to general chemical and physical laboratory purposes.

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[1] Presented at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

[1] Act of Congress, June 7, 1906; amended March 2, 1907; Act, October 3, 1913.

The latter class (completely denatured) promises some needed relief for the liquid fuel shortage and may consume much the largest portion of denatured alcohol. That means denatured alcohol will become even more common that it is now.

Data collected prior to 1918 indicated that the drinking of liquids containing methyl hydroxide was responsible for many deaths and acute cases of blindness.[1] The "deodorized" methanol resembles pure ethanol so closely that the ordinary layman can hardly distinguish the difference between the two. In complex mixtures, whisky, etc., its detection involves very careful chemical analysis. Formerly it cost less than ethanol, so unscrupulous people were tempted to use it as substitute for ethanol in adulterating whisky, essences, extracts, bitters, washes, liniments, balsams, perfumes, etc. The victims were generally those who indulged in the commoner forms of whisky, rum, and wine, although persons not addicted to the use of intoxicating drinks were undoubtedly often affected innocently from drinking Jamaica ginger, lemon extract, essences, bitters, medicines, etc., whose chief menstruum was "deodorized" wood alcohol. At one time the poorer negroes in the Southwest drank it under the name of "white horse" or "old mule." Happily, the abuses grew less through the operation of the National Pure Food and Drugs Act of June 1906. However, during the penumbra of prohibition many cases of blindness and death occurred through the drinking of wood alcohol or denatured alcohol.

The "completely denatured alcohol" is the more readily obtainable. Formula No. 1 called for 10 per cent of specified commercial methyl alcohol with one-half of 1 per cent of approved benzine. This has been, and is, used in radiator water of motor vehicles to make a non-freezing mixture. This may account in part for the cases traced to garages. After the outbreak referred to, this formula was revoked December 29 last, appearing in orders issued January 8, 1920. Hereafter no completely denatured alcohol containing more than 2 per cent methanol will be allowed. As alcohol of strengths above 80 per cent require dilution before drinking, it is doubtful if any future acute cases may be attributed to denatured alcohol, that is, after the present outstanding stocks under Formula No. 1 are used up.

However, we cannot be so hopeful in regard to chronic cases culminating in blindness or defective vision which may be attributed to drinking diluted denatured alcohol containing methanol. The denaturing deterrents are selected primarily on account of the nauseous odor and repulsive taste, rather than physiological action. These odors and tastes repel some people. "Rot gut" whiskies and some "mountain dews" are not far behind varieties of denatured alcohol in odor and taste. With added flavoring, denatured alcohol containing 2 per cent of methanol may be diluted until it contains 1 per cent or less of methyl hydroxide, and be drunk. Death is not to be expected, immediate nor early blindness, from such a draught. And therein lies the danger, so apparent to all who are familiar with the cumulative action of drugs and the insidious influence of liquor.

Proper doses of paraldehyde produce some physiological effects associated with ethyl alcohol. It has been stated, but not authoritatively supported, that paraldehyde was shipped to Russia from another country (not the United States) to serve as a substitute for vodka. We are familiar with the historic accounts of ether sprees indulged in by the Irish and "Picadilly Willies," and recent medical literature tells of the successful use of oil-ether cocktails prior to dressings of seriously wounded soldiers. So a variety of intoxicants and exhilarating soporifics are actually available, but their names and associations are those of *drugs*, hence their use is not common. If we can but divorce the name and promote the recognition that these "-ol" bodies are in fact drugs and dangerous, liable to produce blindness, the very element of fear alone will have a most salutary effect in protecting men and women from themselves.

Producers of 90 per cent of the refined methyl hydroxide in this country have decided that hereafter all packages containing it shall be labelled "methanol," and so their advertisements read in the trade journals this day.

This change in nomenclature has been recognized, but the usage cannot be brought about instantaneously and will require time. The word will continue as a synonym in any event, although through concerted action it may become more or less obsolete. No form of legislation can eliminate the name. This is an appeal to chemists to assist.

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[1] See extensive report to the New York State Factory Investigating Commission, 1913, by the author.

SCIENTIFIC SOCIETIES

NATIONAL RESEARCH COUNCIL

REPORT OF THE CHAIRMAN AT THE ANNUAL MEETING OF THE DIVISION OF CHEMISTRY AND CHEMICAL TECHNOLOGY

The work that the Division of Chemistry and Chemical Technology has done during the past year has been set forth in the reports of the chairmen of the various committees.[1] It is now desirable to consider questions of general policy for the future. The regular committees of the Division have done good work during the past year and there is every reason to suppose that the newly-appointed committees will do equally well during the coming year. While this is gratifying, it is not enough, because research work in chemistry is in a fairly satisfactory state quite apart from the National Research Council. If we are to justify our existence, we must get important results which would not have been obtained except for the efforts of the Division of Chemistry and Chemical Technology.

The most obvious, and I believe the wisest, thing to do is to develop the borderlands between chemistry and one or more of the other sciences. These fields are not being developed at present in spite of the fact that modern physical chemistry shows what can be done along such lines. The conditions at Washington are particularly favorable for such a development, because the chairmen of the different divisions are under the same roof and can discuss matters informally in a most satisfactory manner. It is easy to see that if we bring together three men representing three different sciences, and if each man knows a quarter of a given problem, the problem is three-quarters solved before any further work is done. While the thing is not always as simple as that, there are many problems which can be solved only with great difficulty, if at all, by any one man, and which can be attacked best by two or more men representing different sciences.

I have jotted down a few of the borderland problems which happen to interest me. Some are important ones and some are relatively unimportant. Another man would probably make out a different list, but this one will illustrate what I have in mind.

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[1] Abstracted in This Journal, 12 (1920), 711.

BAKING

The American Institute of Baking has recently been founded, with Dr. H. E. Barnard as director and Dr. Morrison in charge of research. Since the problems of bread making require a great deal of special knowledge, an Advisory Board has been appointed, consisting of Messrs. Bancroft, Barnard, Clowes, Henderson, McClung, McCollum, Mendel, Mendenhall, Morrison, Marlin, Prescott, and Taylor. One of the first problems to be undertaken will be that of gluten. It is known that, in general, flour with more gluten makes a better loaf than flour with less gluten. On the other hand, there are certain flours with a relatively low gluten content which make fully as good loaves as other flours with larger amounts of gluten. To account for this the bakers have assumed the existence of strong and weak glutens; but this does not seem consistent with the fact that the different glutens all appear to have the same chemical composition. It is not known whether the differences are due to structure or to the salts present. Staleness in bread is apparently due to a displacement in the distribution of the water content between the gluten and the starch, and it is an interesting problem in colloid chemistry to see whether this can be prevented in any easy and economical way. Although the bakers use a better grade of flour than the housewife, bakers' bread in America is not as good as the best home-made bread. This cannot be due to the baking on a large scale, because French bread is better than ours and Vienna bread is still better. It ought not to be difficult to formulate the conditions for producing any desired quality of bread on a large scale. Improbable though it seems to the chemist, it is said that nobody has ever made use of the microscope in studying bread and bread making. In the case of bread problems, the organization has been provided and we can now await results.

TURPENTINE

In other cases we are not as yet so fortunate. When the change was made from the box to the cup method of tapping trees for turpentine, the total yield for the year was greater by the latter method; but the flow was less during the early spring months until after six or seven weekly chippings. Tschirch's experiments on the development of resin ducts seem to account for this. In the untapped pine, the resin ducts occur scattered through both the heart wood and the sap wood, but in a very limited number, varying in different trees of the same species. These resin ducts he calls primary resin ducts, and the resin which flows from them when they are cut is a purely physiological product. The flow from such primary resin ducts is extremely limited, but after a tree is wounded there at once begins, according to Tschirch, in the outer sap wood a formation of numerous and much larger secondary resin ducts from which crude turpentine pours out over the wounded surface as a healing balsam. This resin is a pathological product. These secondary resin ducts constitute the chief source of commercial crude turpentine and form both above and below the wounds, the length of the ducts above the wound being greater than of those below it. Viewed in a longitudinal tangential section they appear as a network of tubes. Gradually the mouths of these resin ducts become clogged, presumably from oxidation and crystallization of the resin, and the flow ceases. Hence the necessity of chipping to re-open the ducts.

In the light of Tschirch's discovery concerning resin flow, the explanation of the shortcoming of the cup system is apparently very simple. Under the box system, the box is cut during the winter months and the trees are cornered in the late winter giving wounded surfaces. The trees usually stand for several weeks without further wounding, during which time the formation of secondary ducts presumably begins at all points of the cut. Later, when the tree is chipped, these secondary ducts are opened along the full length of the cut and a good yield is obtained at once. When the cups were placed during the winter, it was at first the practice to make with the broad axe two flat faces meeting at the center. The cuts for insertion of the gutters were made on these faces, the upper portions of which had oval outlines. The formation of the secondary resin ducts presumably begins at once and continues during the succeeding weeks, following the outline of the curved upper edges of the faces. At the beginning of the chipping season the first chipping is made from each side to the center, the outer edge being considerably higher than the center. The result of this is that only the secondary resin ducts near the center of the face are cut, and consequently the bulk of the resin flow during the first few weeks of chipping comes almost entirely from this limited central area. Assuming the correctness o this theory, the solution of the difficulty is extremely simple. When the gutters are placed upon the trees during the winter months, the chipper should make a regular chipping the full width of the face to be scarified during the following season. Then the vertical secondary resin ducts would be formed along the entire length of this cut and the first regular chipping in the spring would open the full number of these ducts.

During the winter of 1906–1907 this theory was presented by Dr. Herty to a number of turpentine operators who were using the cup system, with the request that they test its correctness. In every case the tests were thoroughly successful, the yield from the first chipping exceeding that from cups placed without the winter chipping or from boxed trees which had been cornered. The same explanation accounts apparently for the common experience among turpentine operators that boxes cut very late in the winter do not give a good yield during the early spring. The shortcoming is not due to the lateness of the box cutting, but to the consequent lateness of the cornering and to the fact that there is not time enough before chipping begins to permit the full formation of the secondary resin ducts above the cut made in cornering.

While the application of Tschirch's views on resin flow was successful in overcoming a practical difficulty and in increasing the flow of oleoresin, later work has shown that the working hypothesis was unsound, even though it was apparently confirmed by the experimental results. In the spring of 1916, Miss Gerry, of the Forest Products Laboratory at Madison, Wis., went to Florida to study microscopical sections of wood of pine trees just brought into operation, and of trees which had been tapped for one or more years. Miss Gerry's work showed clearly that while secondary resin ducts are formed in the wood as a result of wounding the tree, these ducts do not appear in the spring wood, but only in the summer wood, their formation occurring approximately in July. We are, therefore, left without any explanation of the true cause of the shortage of resin flow in the cups as originally placed on the trees or of the elimination of this shortage by making a preliminary chipping during the winter. It is, therefore, quite possible that some other method of stimulating the tree might be more effective, both as to yield of turpentine and as to length of life of the tree. The solution of the problem appears to involve coöperative work by a botanist, a microscopist, an organic chemist, and a colloid chemist. Since the turpentine industry is now on a purely empirical basis, it is quite possible that a scientific study of this problem might lead to a revolution in the present practice of turpentine gathering.

The problem is not an isolated one. In the tapping of rubber trees the phenomenon of wound response is a familiar one and it is quite probable that any information obtained from a study of the flow of turpentine could be applied with few modifications to the collection of rubber. Shellac is a purified resin which exudes from certain trees after they have been stung by certain insects, especially the cochineal insect. This seems rather a primitive way of extracting resin.

PROTOPLASM

The work in colloid chemistry on the conditions determining whether an emulsion shall be of the oil-in-water or the water-in-oil type has already proved of service in biology. Clowes has been able to offer a satisfactory explanation of Loeb's work on the antagonistic action of calcium and sodium salts. By impregnating filter paper with an emulsion of oil, water, and soap, to which he afterwards added sodium and calcium salts, Clowes has been able to duplicate quantitatively Osterhout's experiments on the specific electrical conductance of certain tissues. While of course nobody believes that protoplasm consists of water and olive oil or kerosene emulsified by a mixture of sodium and calcium salts, there is no denying that in some respects protoplasm behaves like such a simple system. It is evident that this analogy should be pushed to the limit as a working hypothesis, so that we can know just what properties of protoplasm can be accounted for in this simple manner.

WAR GASES

It has been shown that "mustard gas" is not toxic in itself, but that it penetrates the cell readily, owing to its high lipoid solubility. It is then hydrolyzed inside the cell, setting free hydrochloric acid, which is the real destructive agent. Hydrochloric acid itself does not penetrate the cell walls readily and the function of the mustard gas is, therefore, to provide for an intracellular liberation of the hydrochloric acid. According to this hypothesis, the important factors in determining the action of mustard gas, or of any other gas which acts similarly, are the lipoid solubility, the water solubility, the volatility, and the rate of hydrolysis.

If a substance hydrolyzes practically instantaneously, as is the case with arsenic trichloride, there is no chance of the hydrochloric acid passing through the skin. If a substance is very volatile, a good deal of it may evaporate from the skin before it has time to penetrate. If a substance does not penetrate the skin or the cell wall, no hydrochloric acid can be set free inside the cell, and we shall not get the effects characteristic of hydrochloric acid inside the cell. Phosgene, for instance, is very volatile and does not penetrate the skin readily, and consequently does not produce burns. The more unprotected the tissue the more easily will phosgene pass through, and consequently we get the maximum effect from phosgene at the base of the lungs where the tissues are the most permeable. On the other hand, mustard gas is not very volatile and passes fairly readily through the skin. Consequently it causes burns. Owing to the readiness with which it passes into the tissues, it is taken up in the throat and the upper part of the lungs, causing burns there rather than farther down, as is the case with phosgene. This is undoubtedly the reason why a man gassed with mustard gas loses his voice temporarily. Owing to the low rate of hydrolysis, a low concentration of mustard gas may be swept out of the tissues at the base of the lungs by the blood stream before any appreciable hydrolysis takes place. This factor accentuates the difference between mustard gas and phosgene.

A substance with intermediate properties will, however, show some of the characteristics of mustard gas and of phosgene. This is true with phenyldichlorarsine and ethyldichlorarsine, both of which have low vapor pressures, fairly high rates of hydrolysis, and high lipoid solubility. They, therefore, attack the skin and upper respiratory tract as does mustard gas, and also cause profuse edema in the lower respiratory tract as do phosgene and superpalite. Of course, the arsenicals may also have a specific toxic effect due to the arsenic content, but there is no danger of confusing this with the effect due to hydrochloric acid.

While the behavior of phosgene, mustard gas, and phenyl dichlorarsine is what it should be, superpalite is more toxic than one would expect from its known rate of hydrolysis, and it is possible that there may be an intermediate formation of phosgene. We do not know at all why the tear gases act as they do, and any hypothesis will have to account for the two facts that in general the bromine compounds are more lachrymatory than the corresponding chlorine compounds, and that one particular chlorine compound is as effective as any bromine compound. Since this chlorine compound is extraordinarily persistent, it does not seem probable that any ordinary hydrolysis can be involved.

These war-gas problems are interesting in themselves; but their real importance is that they open the way to a study of the chemistry of blisters and burns, and because they lead up to the general study of chemotherapy, a subject of tremendous value which can be developed only by coöperative work between medical men, biologists, and chemists.

SPECIAL SUGARS

It has been shown that it is possible to differentiate bacteria by their ability to decompose some of the rarer sugars. This is a double-barrelled problem because it is necessary for the chemists to prepare these sugars in a high state of purity so that the tests of the medical men may be significant. Then, too, the chemists will wish to determine to what extent different bacteria will decompose a given sugar in different ways. For this the medical men will have to furnish the chemists with colonies of guaranteed bacteria.

NORMAL WEIGHT

The general belief among physicians appears to be that variations in body weight depend directly upon the variations in food and exercise. This can be written $dW = dF - dE$, where W, F, and E are weight, food, and exercise, respectively. In this form it looks like the first law of thermodynamics, and is correspondingly impressive. In order to account for the remarkable constancy of body weight in many cases, it is assumed explicitly that the regulation is due to variations in the appetite. This general belief does not seem to be supported by the facts as I know them. It is a very difficult matter to fatten a thin man, and even if one succeeds by great efforts the extra weight comes off with great promptness. Stock raisers appreciate this, and they breed beef cattle, realizing that it is money wasted to try to fatten scrub steers. The case of the fat man is simpler because he can be brought down in weight by cutting down sufficiently on his food or by increasing the amount of exercise. The experiment has recently been tried on a large scale in Germany. It is not such a simple matter, however, as one might suppose, and I am quite sure that the medical men are on the wrong track.

It seems to me that all the evidence available points to the conclusion that at any given moment any given person has a definite or normal body weight which he tends to hold and from which he does not vary much unless there are large variations in the amounts of food and exercise. This accounts for the facts that it is practically impossible to fatten a normally thin man, and that it is difficult to reduce the weight of a normally fat man. While the latter feat can be accomplished it is liable to be injurious, unless done very carefully, and it is almost certain to be weakening at least temporarily. This is what one would expect if the system were opposing the change, but it is not what I should expect according to the ordinary point of view.

If these premises are admitted, it follows that there is some regulatory mechanism tending to keep the body weight at the normal value, just as we know that there is a regulatory mechanism tending to keep the body temperature at a normal value. There is an enormous difference in the effect of additional amounts of food and water when a man is at his normal weight or is below it. If a man has been dieting so that he is six or seven pounds below his normal weight, the relation postulated by the physicians holds very closely, and an additional chop will have an effect on the body weight. The difference in the two cases is so marked that it seems incredible that physicians should have ignored it. On the other hand, we know that the normal weight, as defined, may change very markedly after sickness or after a sufficiently prolonged dieting. After typhoid, thin people are very apt to increase in weight. Many people increase markedly in weight as they grow older. While this latter change is often due largely to increased food consumption and decreased exercise, that is probably not the whole explanation, because there are many cases where this increase in weight does not take place.

The changes after sickness and after prolonged dieting show that it is possible to change the regulator. If we could do this voluntarily and easily, people could be kept, without difficulty and without danger, at any body weight which was not inconsistent with the bones and muscles of the individual. This would be of tremendous importance medically, in view of the fact that the life insurance companies have shown that the man of average weight has a better chance of life than a man who is distinctly above or distinctly below average weight.

At present we have no clue as to what the regulatory mechanism is. The phenomena of growth and development evidently depend on the interrelation of the activities of the thyroid gland, the gonads, and the hypophysis; but Professor Stockard tells me that feeding thyroid extract is sometimes effective only temporarily because the thyroid gland may cut down its activities in consequence. This shows that the regulatory mechanism is farther back. This is also shown by the fact that intense activity of the gonads should so monopolize the thyroid as to leave the effect due to the hypophysis unbalanced, and so cause an increase in weight. Actually the activity of the thyroid is increased.

It has been shown that the water-soluble vitamines are of great importance in determining the body growth of young animals, and it is of course possible that the normally thin man contains something in his system which is more or less toxic to the particular vitamines which may be responsible directly or indirectly for the increase in body weight, but this is nothing more than an interesting suggestion at present. It seems to me that the first thing to do is for the medical men to recognize definitely and officially the importance, as a scientific problem, of the determination whether there is a mechanism which regulates the body weight and, if so, how it functions. The problem itself is one in the borderland between medicine and chemistry which can probably be solved only by coöperative work. The chemist cannot do it single-handed, and there is no evidence that the medical man can. Fortunately, it is not the province of the scientific man to decide whether it is really desirable, apart from the question of comfort and longevity, to promote the physical standardization of man.

The question of the water equilibrium in the body is a subsidiary one which is possibly easier to solve and which undoubtedly has a very important bearing on the broader question. When a man is at his normal weight, he can drink practically as much water as he pleases without producing anything more than a temporary increase in weight. If he takes violent exercise or decreases his water consumption until there is a loss of weight of several pounds, practically all of it water, the amount lost will be regained and retained if an excess of water be drunk. I have known of a permanent increase in weight of eight pounds in ten minutes through drinking a great deal of water after carrying the weight that much below normal. Sweating off weight is an inefficient method of reducing, because most of the loss is regained if a man drinks water and he is liable to develop kidney trouble if he stints on water. If, however, a man's weight is reduced ten or twenty pounds by dieting and is kept there until the hypothetical regulator has become adjusted to the new figure, drinking an excess of water will not cause a permanent increase in weight, though it will do so if the water is drunk before the regulator has become adjusted to the new position. We do not know what determines the amount of water that the tissues will take up, and we do not know whether there is a change in the amount of water that the tissues will take up or whether tissues burn up more readily when partially dry. In any case, the regulation of the body weight is evidently connected closely with the problem of water equilibrium in the body. Fortunately, this latter problem is now being studied carefully by Professor Mendel and others.

The question of water equilibrium is also of distinct interest to the botanist. Professor Duggar has recently pointed out that the water relations of cell or tissue, as governed by diffusion and colloidal hydration, constitute an important problem for joint research. "On present information the plant physiologist may have no idea of discarding the role of osmotic pressure in the cell, but it is to be inferred that he is in full sympathy with the proper evaluation of this factor, and he could well join forces with the physical chemist to examine critically and in a new light all factors involved."

STRUCTURAL COLORS

We distinguish between pigment colors and structural colors. In the latter case the particular color is not the result of absorption by a colored or pigmented substance. The colors of the rainbow, of the blue sky, of snow, and of thin films are instances of structural colors. These structural colors are of great interest to the biologists and have been studied extensively by them, but there is still much work to be done. We know that the white color of snow, of hair, and of the lily is due to the scattering of light by enclosed air-bubbles; but we are not certain about birch bark or about the white bark of the sycamore. We know that the color of the blue eye is not due to pigment and that it is undoubtedly the blue of turbid media like the blue of the sky; but there is still some question as to the extent to which the color of the uvea plays a part. There is no question but that the green of the tree frog is due to the superposition of a yellow pigment on the blue of a turbid medium; but nobody has duplicated this synthetically. We know that there is no blue pigment in the feathers of such birds as the bluebird, the indigo bunting, the blue jay, and the kingfisher, and it is probable that the blue is the converse of the blue of the sky and is due to the scattering of light by myriads of minute air-bubbles in the horny mass of the feather; but this view is not held by most biologists, and nobody has as yet made a blue feather in the laboratory. Michelson has shown that the metallic colors of some butterflies and beetles are due to surface colors from solid pigments analogous to magenta; but these pigments have not yet been isolated. In a great many cases we know that we are dealing with structural colors; but the exact mechanism of the production of the color has not been established conclusively. It is very desirable that an exhaustive study should be made of structural colors in nature.

One case is of special interest because no satisfactory explanation has yet been given. After certain volcanic outbursts, the disk of the sun is seen to be blue or green in the morning or evening. There seems to be no question but that the phenomenon is connected with the volcanic outbreaks and is, therefore, due to the presence of gases or dust from the volcano. The difficulty is that fine particles should cause a scattering of the shorter wave lengths, and should make the disk of the sun red and not green or blue. Tyndall pointed out years ago that the disk of the sun appeared green and not red, when looked at through thin plates of an unspecified brownish black glass. The volcanic dust is a brownish black glass and might correspond to Tyndall's unknown glass, in which case everything would be very simple. This is a question of fact, however, and has received no support so far from the geophysicists. Another line of attack is suggested by the fact that the disk of the sun appears reddish, as it should, when looked at through a freshly made photographic emulsion, consisting essentially of gelatin and silver bromide. If this emulsion be ripened, however, the disk of the sun appears bluish green. Since this experiment can be repeated and varied without difficulty, there ought to be no trouble in working out the theory of it, though this has not yet been done.

SEDIMENTARY ROCKS

Some of the geologists are very anxious to secure the establishment of an institute for the study of sedimentary rocks, which would take the place in this field that the Geophysical Laboratory takes in the field of igneous rocks. If such an institute can be established, the coöperation of the chemists will be essential to success. While the geologist knows about the occurrence, composition, general properties, etc., of the sedimentary rocks, the chemist will have to assist in all matters of solubility, coagulation, and agglomeration, rate of settling, etc. The work should be tied in with that done on the thickening and settling of ore pulps. There is one striking illustration which brings out clearly our ignorance on certain points. Although there are cubic miles of dolomite in the Dolomitic Alps and elsewhere, nobody has ever made any dolomite in the laboratory.

CLAY

In spite of all the work that has been done on the plasticity of clay, it must be admitted that we have no satisfactory theory in regard to the subject, and yet it is a problem of wide-spread interest. The ceramists wish a clay that is plastic, while the farmer wishes the contrary. There seems to be no question but that the plasticity of clay is due in large part to the presence of a gelatinous film round the clay particles, but we do not know at all what it is that prevents these gelatinous films from losing their power to take up water after being dried in the sun. The problem does not appear to be a difficult one, but it has never been attacked by anybody having an adequate theoretical knowledge, because colloid chemistry has hitherto been on so empirical a basis.

There are a number of other questions in regard to clay which are of interest to the geologist, the chemist, and the ceramist. Sillimanite, anorthite, albite, and orthoclase are apparently definite compounds, but when the feldspars weather to a so-called kaolin, is that kaolin a definite compound or not? Mellor believes that kaolin breaks down into alumina, silica, and water at about 500°, but he has furnished no conclusive proof of this, and Klein's optical studies do not confirm it. The catalytic action of kaolin on alcohol is practically identical with that of alumina and quite different from that of silica. Clowes has found some interesting results on adsorption by different clays which had not been predicted by anybody. It is quite clear that there must be a new and careful study made of clay, coördinating the chemical, optical, catalytic, and adsorptive properties. The study of the properties of fired clays would include the chemistry of the pigments in glasses and glazes, a matter on which we are woefully ignorant.

PRESSURE PHENOMENA INSIDE THE EARTH

There is apparently some evidence that at high pressures in the earth, oil and gas may be formed, although this is the system occupying the larger volume. Of course, this cannot occur if we are dealing with reversible equilibrium and a uniform pressure. It may occur, however, if we are not dealing with equilibrium relations or if we have differential pressures. This latter problem is interesting in itself quite apart from any possible geological application. If we take hydrated sodium carbonate or sulfate and put it under a high nitrogen pressure, there is a high pressure on the hydrated crystal, while the partial pressure of the water vapor remains theoretically the same. It should be possible, therefore, to squeeze the water out of the hydrated salt. Similar results should be obtained, though less easily, with copper sulfate and with gypsum. One could then, perhaps, decompose oxalic acid by differential pressures and thus open up a new field of chemistry. Dr. Adams of the Geophysical Laboratory is interested in this problem.

One thing that bothers the geologists is that the earth behaves like a rigid body, transmitting transverse vibrations in spite of the high temperature which is ordinarily believed to occur at the center of the earth. There are two possible explanations of this and the chemists ought to coöperate in deciding between them. Owing to the high pressures the center of the earth may actually be solid in the strict sense of the term. It may be crystalline. On the other hand, the geologists call glass a solid because it transmits transverse vibrations, while the chemist considers it strictly as a supercooled and very viscous liquid. Now, we know that increasing the pressure on water increases its viscosity. If this is a general phenomenon, a sufficient pressure on molten glass would make it as viscous as glass at ordinary temperature. So long as we are speculating, there is no reason for stopping here. If increasing the pressure increases the viscosity, there is no apparent theoretical reason why carbon dioxide or even hydrogen might not become sufficiently viscous under high pressures to transmit transverse vibrations even above the critical temperatures.

THUNDER STORMS

Simpson has developed a theory of thunder storms which seems to be the best available, though it is by no means accepted universally. He assumes the existence in the center of the storm of a rapidly ascending current of air which spreads out and loses speed above a certain height. Large rain drops will fall through this air current until they reach a point where they are broken into smaller drops, and are then carried to the upper and colder levels where they grow again and repeat the cycle. When the drops break up they become charged positively, while the negative ions are carried up more rapidly by the air and are finally caught by cloud particles at some higher level. Simpson satisfied himself that the electricity generated by the breaking up of the falling drop might easily account for the gradient of 30,000 volts per centimeter necessary for lightning. If we could make a synthetic thunder storm in the laboratory by means of a blower, it would enable us to test Simpson's theory in a way that cannot be done now, and it would probably be of great interest in other meteorological problems. If we change from flashes of lightning a mile or so long to flashes an inch long, the other dimensions of the thunder storm could be decreased considerably, though we do not know to what extent. It is a problem in mathematical physics to determine approximately the minimum theoretical size of a thunder storm. Professor Barus of Brown University has interested himself in this matter and some day we shall know whether a synthetic thunder storm can be handled satisfactorily in a physics laboratory. If that problem can be solved successfully, it will then be interesting to consider the possibility of synthetic hail storms.

SURFACE COLORS

The data in regard to the colors of colloidal solutions of gold, silver, copper, and indigo make it seem probable that very fine suspensions of substances showing marked selective reflection of surface colors transmit, presumably by resonance, the colors which they ordinarily reflect the most strongly, and scatter the colors which they ordinarily transmit the most readily. With coarser particles or with films the phenomenon is reversed. This will have to be tested with a number of organic pigments showing marked surface colors so as to see whether the generalization is really sound and universal. If so, it will then be for the physicists to work out the optical theory of the phenomenon.

BROWNIAN MOVEMENTS

Einstein has deduced a formula for the viscosity of a suspension of rigid spheres in any liquid, in terms of the viscosity

(η_1) of the pure liquid and the ratio (f) of the volume of the suspended matter to the total volume.

$$\eta_1 = \eta(1 + kf),$$

where k is a constant which Einstein at first considered equal to unity, but which he afterwards made equal to 2.5. A similar formula has been deduced by Hatschek for cases where the suspended material occupies less than 40 per cent of the total volume. It differs from Einstein's formula by having $k = 4.5$. According to these formulas the viscosity depends only on the volume of the dispersed or suspended phase, and not on its degree of subdivision, there being no term for the diameter of the solid particles. Odén found, however, that solutions of colloidal sulfur containing particles of suspended sulfur of $10\mu\mu$ diameter were 40 to 50 per cent more viscous than otherwise identical suspensions in which the sulfur particles had a diameter of about $100\mu\mu$. Hatschek believes that the discrepancy between experiment and theory is due to the fact that the sulfur particles have on their surface a film of adsorbed or condensed water which should properly be considered as part of the volume of the particles. He shows that the discrepancy disappears if we assume an adsorbed film having a thickness of about $0.9\mu\mu$, which is certainly not unreasonable.

If we assume no adsorbed film, the mathematical treatment leads to the conclusion that the viscosity is independent of the diameter of the suspended particles, and depends only on their total volume. If we assume an adsorbed film, even one so thin as $0.9\mu\mu$, we draw the conclusion that the viscosity increases with decreasing size of the suspended particles, a very different conclusion.

Einstein has also made a study of the so-called Brownian movements of colloidal particles suspended in a liquid, and has deduced formulas that lead to a very interesting set of relations, which are apparently confirmed fairly well by the experiments. He has not considered the possibility of an adsorbed film on the particles, and it seems very desirable that some mathematician or mathematical physicist should go over his work and see to what extent the assumption of an adsorbed film of some definite thickness would modify the conclusions reached. The error was so serious in the case of the formula for the viscosity that it is not safe to assume that it will be negligible in the equations for the Brownian movements.

There is another matter about the Brownian movements that needs clearing up, presumably by a mathematical physicist. Perrin found that, with gamboge particles a little over 0.4μ in diameter, each rise of 30μ caused the equilibrium concentration to fall to one-half its previous value, while a difference of 6μ produced the same effect when the gamboge particles were about 1.0μ in diameter. On this basis the concentration at the top of a beaker 6 cm. high would be only $1/2^{2000}$ of that at the bottom in the case of the fine particles. This does not harmonize at all with the fact that the color of a colloidal gold solution is nearly uniform over the whole height. Either the gold solution will settle in time, or there is something wrong with Perrin's mathematics. Professor Burton of Toronto University suggests that perhaps the concentration increases under the influence of gravity as lower levels are reached in the beaker up to a certain value, after which the concentration remains practically uniform. It is very desirable that the actual facts should be determined, and that the mathematical theory should be revised in case it proves to be wrong.

ADSORPTION OF GASES

It is sometimes stated that a liter of carbon black contains two liters of air, and that the carbon black occupies only five per cent of the volume. If this is true, a complete removal of the air should cause a tremendous change in the apparent volume of the carbon black. Experiments of this sort are needed, partly as proof of the presence of adsorbed air films, but more because Bingham has brought forward evidence for a very interesting relation between the apparent voids in a powdered solid and the amount of liquid necessary to produce zero fluidity. If Bingham's relation holds absolutely, the volume of the adsorbed air film must be the same as the volume of the adsorbed water film, which may be true, but which seems improbable.

CRITERIA OF PURITY

In order to isolate and utilize the constituents of coal tar we must prepare the compounds in a pure state and determine their properties. This is not so simple as most people imagine. The correct melting point of anthracene is probably known to but few in the United States. The melting point of carbazole, as given in the literature, is in error by 7°. The melting points of mixtures of carbazole and anthracene are probably known to but one or two laboratories in this country. In order to have adequate tests for purity, the organic chemist must be ready to make use of any of the physical constants, because no one can tell which one will be most sensitive to traces of impurity. Even the form of the melting point or solubility curve, as predicted by thermodynamic theory, can serve as an index of the purity of the material. There is good reason to believe that the magnetic rotation, dielectric constant, critical data, and especially the electric and magnetic birefringence will be valuable criteria of purity. This means that the physicist and the physical chemist must coöperate with the organic chemist to devise rapid and moderately accurate methods of determining physical constants. At present very few organic chemists make use of the colorimeter, spectroscope, spectrophotometer, interferometer, etc. The colorimeter is the right instrument to use in standardizing colors. In a few minutes one can get a report, using only solvent, dye and the instrument, whereas the common practice in dye laboratories calls for expensive wool, cotton, and silk yarns, many helpers to weigh and dye the yarn and to mount, with a report available only after a delay of 24 to 30 hours.

The spectrophotometer is almost the only quick way of detecting commercial mixtures and frauds and it will do more in giving a quantitative correlation of color and structure than any other instrument. Once the necessary mass of data has been accumulated, scientific color making will become an actuality. In spite of this nobody has designed a spectrophotometer for the special use of the organic chemist. Somebody must do for the spectrophotometer and other instruments of the physicists what has already been done for the polariscope. W. P. White of the Geophysical Laboratory has recently written an article showing how certain conclusions in regard to purity can be drawn from a study of cooling curves, and T. R. Briggs of Cornell University has developed a quick and easy method of telling whether mixtures of two liquids do or do not give a maximum or minimum boiling point. These are excellent pieces of work, but they constitute an infinitesimal portion of what should be done.

QUICKSANDS

The quicksand is a well-known stage setting in novels and books of adventure, and it is also a well-recognized metaphor, but our scientific knowledge in regard to it is extremely limited. It is not easy to find who should know about quicksands. It seemed to me at first that the subject was a problem in physics; but the Department of Physics thought otherwise, and said that quicksands belonged under geology. The Department of Geology was mildly interested, but disclaimed all knowledge, saying that quicksands should be studied under physical geography. The Department of Physical Geography found no reference to quicksands in its standard books and advised me to interview the mineralogists who, of course, knew nothing about the subject but advised me to consult the engineers. The Department of Civil Engineering said that engineers were familiar with methods of handling quicksands, but that they had never been interested in the theory of the subject. I found later that this last statement was not accurate. Somebody suggested that quicksands were soils, and I therefore wrote to a Washington bureau, asking whether it could give me any references to papers on quicksands. In a misguided moment I added that the bureau might perhaps be posted on quicksands because they were infertile soils. I received a very polite letter giving references to five papers on the grading of sand—which had no apparent relation to quicksands—and a reference to Victor Hugo's "Les Misérables." The writer added that quicksands were not in themselves infertile soils, but that they were too full of water for crops to grow well in them. A search through the University library showed that quicksands belong theoretically under forestry. It is a part of the business of the German forester to keep sand dunes from shifting. Since there are often strips of quicksand at the foot of the dunes near the Baltic, the theory of quicksands is discussed to a limited extent in German books on forestry which deal with sand dunes. I have since found one series of papers on the subject by American civil engineers, and there are scattered references to the subject in all sorts of places, but our scientific knowledge of quicksands is extraordinarily meager. It seems to me that this is a subject which should be taken up by the civil engineers, the mining engineers, and the colloid chemists. The mining engineers come in because ore dressing by means of hindered settling is really a special problem under the head of quicksands.

METALLIC LUSTER

At first sight it might seem as though there were few matters in which the chemist could coöperate with the psychologist, but the question of metallic luster is one. Metallic luster is usually defined as the luster of metals, which is a restatement and not a definition. It is also insufficient because an empty glass test tube placed in water and looked at so as to give total reflection is more metallic than mercury itself. If we combine a black image on a white ground with a white image on a black ground by means of a stereoscope, we get a metallic luster instead of a sensation of gray. A similar effect is produced if we combine a yellow image on a blue ground with a blue image on a yellow ground. These experiments show that the problem is a psychological one in some cases, and possibly in all. The psychologists were in the habit of giving experiments with metals, with total reflection, and with the stereoscope to show the different ways in which the sensation of metallic luster could be produced, but they stopped there. A tentative theory has recently been developed, chiefly by Dr. Buckingham of the Bureau of Standards. It seems probable that we get the sensation of metallic luster whenever we have a nervous flutter or unsteadiness of attention, as when one combines two pictures having different degrees of brightness. The element of fatigue enters in very largely and, as a matter of fact, some people are much more sensitive than others to binocular luster, as it is called. Woolen goods striped black and white appear lustrous to a few people, though not to most. This seems to be an exaggerated case of the eyes wandering over the surface in a jerky manner. With metals there is reflection from the surface and from a plane only just below the surface, giving rise to the flutter effect. When looking at a thing which is not itself a metal, the sensation of metallic luster will be attained more easily if the texture of the surface of the material resembles that of a metal. We also get the sensation of metallic luster in cases in which there are simultaneously a roughened surface and a high reflection of light. The most familiar instance of this is the silvery streak which marks the reflection of the moon from a water surface rippled by the evening breeze. The wavelets make the surface of the water seem rough and the accompanying high reflection of light makes the water look metallic, even more metallic than the disk of the moon itself.

Buckingham's hypothesis regarding the production of the sensation of luster seems to combine all the good points of the theories of Dove, Brewster, Rood, Brücke, Helmholtz, and Spring. It takes into account the possibility of great differences in individual observers which had not been recognized specifically by the others, and it has the advantage as a working hypothesis of suggesting a great deal of research work which ought to be done. Dr. Bingham, chairman of the Division of Psychology and Anthropology, has interested himself in the matter and is trying to get psychologists to make the necessary tests. When the question of metallic luster is settled, it will still be necessary for the psychologists and chemists to work out satisfactory definitions for vitreous luster, pearly luster, silky luster, oily luster, waxy luster, and resinous luster.

EDUCATIONAL TESTS

During the war the psychologists under Dr. Yerkes developed special tests which were applied to fairly large groups of medical men and engineers. Speaking broadly the tests in which the medical men showed up well were those in which the engineers did poorly, and *vice versa*. This shows that the tests have some real significance, though not necessarily what that significance is. It is now proposed to repeat these tests with young engineers and medical students just after leaving college and with prospective engineers and medical students before they enter college. This will show whether the observed differences are inherited, are developed in college, or appear as a result of practicing the professions. This seems to me a very important educational development and I hope that similar tests can be made on chemists before long. At present our only method of testing progress before graduation is by examinations, a method which is fundamentally bad. If we can have an independent way of checking our methods of teaching, it will be of enormous value, and the new method is especially important because it is not essentially a memory test. The new method appeals to me very strongly because it may help us to remedy one known defect in our teaching. The small boy is always asking why. He usually asks many more questions than anybody can answer. By the time he has graduated from college, that tendency has ordinarily disappeared pretty completely. When I start a man on research work and suggest that he try certain experiments, he will eventually report that some one of them did not go. When I ask him why it did not go he looks grieved. He thinks that I ought to be satisfied with the statement of fact and yet it is impossible to make satisfactory progress if we do not find out why the experiments did not give results that we apparently had a right to expect. It usually takes me at least a year to get the graduate student into the habit of asking himself why under all circumstances. It is a great waste of time and energy to knock out of a boy in school and college what must afterwards be put back, presumably in an ineffective and unsatisfactory way, after habits of mind are formed to a considerable extent. I do not know when the damage is done, but my guess is that it is both at school and at college. It is probably a result of filling the boy up with masses of facts which he accepts on authority. To overcome or even to counterbalance this defect in our methods would be an educational reform of inestimable importance and the psychologist seems to have made its realization a possibility.

CONCLUSIONS

As I stated in the beginning of the report, this list of problems includes those which happen to appeal to me personally. I shall continue to be interested in them after I retire as chairman, and I shall do my best to push as many as possible of them on to solution. The next chairman will be interested in other problems, and he will continue to push those after his term has expired. By the time this has gone on for five years or so, we shall have a lot of very important problems under way, and some of them will be yielding results. After that everything will be plain sailing and the Division of Chemistry and Chemical Technology will justify its existence many times over. At present we are unfortunately long on promises and short on results, but I have confidence that that will not continue to be the case.

It will probably be asked why the Division of Chemistry should be the one to urge the development of the borderlands rather than one of the other divisions. The only reason for it is that this sort of work appeals to the Division of Chemistry as very important and does not as yet so appeal to the other divisions. The fact that chemistry is the fundamental science may be the reason why the chemists take a broader view than do the representatives of the other divisions. The formation of the National Research Council has put the leadership in science in the hands of the chemists. We must show that we have the ability to take advantage of the situation and the vision necessary to develop scientific research for the best interests of all.

Wilder D. Bancroft, *Chairman,*
Division of Chemistry and
Chemical Technology

Cornell University
Ithaca, N. Y.
June 30, 1920

SETTING THE SCENES FOR THE CHICAGO MEETING

Special Correspondence to the Journal of Industrial and Engineering Chemistry by John Walker Harrington

Chicago, August 20—Chemistry is to be nominated for yet a higher place in the realm of industry at the sixtieth general meeting of the American Chemical Society, to be held from September 6 to 10, inclusive, in this city. This "Reconstruction Meeting," as it is called, has for its slogan, "Increased Production through Chemistry."

The Chicago Section, keenly alive to the possibilities in store, is proceeding with characteristic ability and vigor to make the approaching gathering an epoch-marking event. The air is surcharged with the spirit of far-seeing and forehanded efficiency. Those intrusted with the arrangements have made use of all the observations which they have made at other meetings; and above all they have put into their preliminary work a fund of initiative. The inspiration of pioneers abides with the Chicago Section and permeates the University of Chicago and the Northwestern University, which are coöperating in the colorful program in store.

Dr. Julius Stieglitz

The various parts of the program will have their appropriate settings. The official headquarters at the Congress Hotel, a towering up-to-date caravansary on the lake front and in close touch with sights of a city in which there is so much to be seen, will show forth chemistry as a practical every-day branch of industry. From this convenient point one may go to the huge manufacturing plants, to the stockyards where modern chemistry has multiplied by-products without end, and to looming factories where articles known throughout the land are created on laboratory advice.

Here in the Gold Room, on the morning of Tuesday, September 7, the honorary chairman of the convention, Dr. Julius Stieglitz, and a representative of the Chicago Association of Commerce, will give the addresses of welcome to which Dr. William A. Noyes, the president of the Society, will reply. There will be discourses also on the larger phases of chemistry, delivered by men of national prominence, in which will be shown the services of the laboratory to the advancement of civilization.

The general meeting will be taken up bodily and transported several miles to Evanston for the afternoon session. Special trains on the elevated railroad will be the magic carpets on which the members will be borne from the station at the back of the hotel to Northwestern University, where the meeting will be continued in the wonderfully lighted and well-ventilated Patten Gymnasium, where 10,000 persons can be seated.

Dr. H. P. Talbot will discuss "The Relation of Educational Institutions to the Industries," in which will be summed up the progress which has been made in bringing about coöperation between the university and the plant. Dr. W. A. Patrick will speak on "Some Uses of Silica Gels," and it is likely that there will be one or two other addresses relating to wide applications of chemistry to the increase of production.

All speeches will have been delivered by half past four o'clock in order to make way for an entertainment on lines as delightful as unique, which is planned for that hour. By way of an earnest it may be said that on the marge of the lake at Evanston, weather permitting, or in the gymnasium, weather forbidding, will be given a combined men and women's entertainment and reception, garden fete, and beach party. The program includes an outdoor picnic, dinner and smoker, band and orchestra concerts, and an organ recital. One may swim or dance or sing, just as he or she likes, and in the evening there will be more recreation in the "Gym," in which various lighter qualities of chemistry will bubble to the top. All these diversions are offered as a substitute for that indoor sport traditionally known as a smoker. All the world of the outdoors is open to the devotees of Lady Nicotine, as well as the companionship of the daughters of Eve.

Suitable arrangements have been made for the entertainment of the women guests. The wives of the Councilors are bidden to a theatre party on Monday night while their husbands are discussing the destiny of the Society after the dinner tendered by the Chicago Section. On the 7th there will be special busses to Marshall Field & Company and return, automobiles will be provided for the ladies who wish to go to Evanston, and on the 8th similar conveyances will be in waiting to transport them to the mail order house of Sears, Roebuck & Company.

Speaking of the social features which everywhere punctuate the program of the meeting, there is a restful nook known as the Chemists' Club, only recently founded, where soft lights glow through alabaster lamps and deep-cushioned chairs invite reactions of repose. The club will have luncheon the first day for the members of the Council, and at all times delegates are welcome to the portals of this retreat of the Knights of the Retort.

Kent Chemical Laboratory, University of Chicago

The good-fellowship and hospitality are like bright threads which give color to the fabric of science which will appear anew at the sessions of the divisions and sections to be held on Wednesday and Thursday, September 8 and 9, at the University of Chicago. The campus of the University in the fall of the year is a symphony of green and gold. If the weather be kind, visitors pass backward and forward to the various meeting rooms in the open air. If not, there are connecting corridors, and temporary canopies will be erected. Most of the meetings of the divisions and sections will be held in the Kent Laboratory over which Dr. Stieglitz presides, and where Dr. William D. Harkins and Captain Gerald L. Wendt, his associates, instruct a zealous legion of students.

For those who prefer to give their attention intensively to the scientific papers, the quarters provided in the laboratories of the University are as appropriate as if especially designed for the occasion. In the Kent Laboratory, three large auditoriums with rows of steeply inclined seats, commodious tables, and the necessary lantern equipment are available on the first floor. Other laboratories and class rooms can be utilized, such as those in the Ryerson Laboratory and the Botany Building close at hand, and the finely appointed assembly room in Mandel Hall.

The advance information so far received indicates that the meetings of all divisions and sections will have unusually strong papers. As announced in the preliminary program, the Industrial Division will have a symposium on fuel over which Dr. A. C. Fieldner, of the United States Bureau of Mines, will preside, and where will be discussed such typical subjects as colloids, gasoline economies, and by-product recovery. A symposium on cellulose is announced by the secretary, Mr. H. E. Howe, who recently visited this city with a view to determining whether or not there was enough interest in this branch of chemistry, considering the wide discussion of paper scarcity and the cotton situation, to warrant the founding of a cellulose chemistry section.

Campus at Northwestern University

Patten Gymnasium, Northwestern University

As usual, the rapidly growing Dye Division, which always finds its quarters too small, is looking at the future through the rose-tinted glasses of its energetic secretary, Mr. R. Norris Shreve. He has been making so determined a drive for new members that it is likely when the roll is called that, whatever quarters are assigned to the Division, it will raise the hue and cry after those who have taken away from it the space it requires.

It is likely that the Organic Division, which increased ten per cent in the last year, will loom large and vie in size with the Division of Inorganic and Physical Chemistry. Owing to the proximity of the University of Illinois, where its secretary, Dr. Roger Adams, is formulating an unusual program, the representation from this Division is likely to pass all previous records. For that matter, all of the ten divisions and the two sections which are to hold meetings will be well represented.

Underwood and Underwood

DR. W. LEE LEWIS

The special transportation committee of the New York Section find that they can secure a special car or cars on the New York Central Train No. 3, leaving the Grand Central Station at 8:45 A.M., Eastern Standard Time, Sunday morning, Sept. 5, arriving in Chicago Monday morning at 7:40 A.M., Central Standard Time. The fares, including extra fare, which is $5.18 from New York, for this train, are as follows, together with the Pullman charges:

CITY	Fare	Upper	Lower	Dr. Room	Compartment
New York City...	$40.46	$7.78	$9.72	$34.02	$27.54
Albany...........	31.84	7.13	8.91	32.40	25.11
Schenectady......	31.19	7.13	8.91	32.40	25.11
Syracuse.........	26.10	5.51	6.91	24.30	19.44
Rochester........	22.98	4.86	6.10	22.68	17.01
Buffalo..........	20.31	4.86	6.10	22.68	17.01
Cleveland........	13.19	3.24	4.05	14.58	11.34

A car or cars can also be secured on Train No. 5, Pennsylvania Limited, leaving Pennsylvania Station, New York City, at 11:04 A.M., Eastern Standard Time, Sunday morning, Sept. 5, and arriving in Chicago Monday morning at 9:00, Central Standard Time. The fares, including extra fare, are as follows:

CITY	Fare	Upper	Lower	Dr. Room	Compartment
New York City...	$41.76	$7.78	$9.72	$34.02	$27.54
Philadelphia......	36.96	7.13	8.91	32.40	25.11
Baltimore........	30.97	7.13	8.91	32.40	25.11
Washington......	30.97	7.13	8.91	32.40	25.11
Harrisburg.......	27.76	6.48	8.10	29.16	22.68
Pittsburgh........	18.23	3.89	4.86	17.82	13.77

If members of other sections and the New York Section desire reservations on either of these trains, the committee will be glad to arrange space for them upon receipt of wires to this effect, stating the space desired, together with the necessary remittance. Address F. E. Dodge, *Chairman*, The Barrett Co., 17 Battery Place, New York City.

The local section urges that reservations for transportation and hotel accommodations be made as early as possible. When members reach Chicago they will find that everything within the range of the humanly possible will be done to make their stay a professional and a social success.

SIXTH NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES, GRAND CENTRAL PALACE, NEW YORK, SEPTEMBER 20 TO 25, 1920

PROGRAM

MONDAY, SEPTEMBER 20

8:00 P.M.—Opening address by Chas. H. Herty.
"Coöperation in the Industries," Charles L. Reese.
Sir George E. Foster, Canadian Minister of Trade and Commerce, will speak.
Followed by MOTION PICTURES:
1: "The U. S. Ammonium Nitrate Plant No. 2 at Muscle Shoals." (2 reels) (Courtesy Dwight P. Robinson & Company.)
2: "Modern Packaging Methods." (4 reels) (Courtesy Pneumatic Scale Corporation.)

TUESDAY, SEPTEMBER 21

2:00 P.M.—FUEL ECONOMY SYMPOSIUM.
Chairman's Address, R. C. Beadle (Managing Editor, "Combustion").
"Burning Coal at 100 Per cent B. t. u. Efficiency," W. O. Rankin (Quigley Furnace Specialties Company).
"Saving Fuel by Controlling Chimney Losses," F. F. Uehling (Uehling Instrument Company).
"Fluid Heat Transmission," Alexander B. McKechnie (Parks-Cramer Company).
"Producer Gas and the Modern Mechanical Producer," W. B. Chapman (Chapman Engineering Company).
"Refractory Cement: Life Insurance for a Furnace," F. W. Reisman (Quigley Furnace Specialties Company).
"Preventing Conduction and Radiation Heat Waste," S. L. Barnes (Armstrong Cork Company).
"The Reason for the Fuel Saving in the Dressler Kiln," Conrad Dressler (American Dressler Tunnel Kilns, Inc.).
8:00 P.M.—MOTION PICTURES: Great U. S. Chemical Industries:
1: "The Story of Sulfuric Acid." (1 reel) (Courtesy General Chemical Company.)
2: "The Production of Salt for the Chemical Industry." (1 reel) (Courtesy International Salt Company.)
3: "Perfumes for the World." (Courtesy Antoine Chiris Company.)
4: "A New Chemical Industry: Leather from the Ocean: Fish Leather" (3 reels) (Courtesy Ocean Leather Company and Ford Educational Film Company.)

WEDNESDAY, SEPTEMBER 22

2:00 P.M.—INDUSTRIAL MANAGEMENT SYMPOSIUM.
"Ultra Analysis of Costs," Harrington Emerson (The Emerson Engineers).
"Research in Industrial Conservation," H. E. Howe (*Chairman*, Div. of Research Extension, National Research Council).
"Progress of the American Coal-Tar Industry," Grinnell Jones (U. S. Tariff Commission).
3:00 P.M.—MATERIALS HANDLING SYMPOSIUM.
Chairman's Address, Roy V. Wright (Editor, "Material Handling Cyclopedia").
"Material Handling: The Paramount Problem," J. H. Leonard (Editor, "Freight and Terminal Engineering").
"Chain Power Transmission," F. G. Anderson (Morse Chain Company).

"Steel Collapsible Shipping Containers as Related to the Chemical Industries," Everett W. Morgan (Pneumatic Scale Corporation).

8:00 P.M.—Meeting of Chemical Warfare Post.
(Speakers to be announced.)

Thursday, September 23

2:00 P.M.—Chemical Engineering Symposium.
(Meeting of the American Institute of Chemical Engineers, David Wesson, *Chairman*.)
"A New Method of Destructive Distillation," Thomas W. Pritchard (Fuel Products Corporation).
"Nitration of Hydrocarbons," A. Hough and W. Savage.
"Recoverance: A Physical Property in Material and Its Importance," Robert G. Guthrie (Widney Test Laboratories).
"Operating Data of a Modern By-Product Coke Oven Plant," C. R. Bellamy.
"Canada and the Chemist," C. Price-Green (Canadian National Railways).
"Utilization of Peat" (illustrated), B. F. Haanel (Canada Department of Mines).
"Corrosion of Iron and Steel as Affecting the Industries," W. D. Richardson (Swift & Company).

6:30 P.M.—Dinner of American Institute of Chemical Engineers at the Technology Club.

8:00 P.M.—Motion Pictures: Great U. S. Chemical Industries:
1: "Modern Coke and Gas Manufacture." (3 reels) (Courtesy The Koppers Company.)
2: "The Story of Petroleum Oil." (3 reels) (Courtesy Standard Oil Company of New Jersey.)
3: "The Asphalt Paving Industry." (1 reel) (Courtesy Barber Asphalt Paving Company.)
4: "Colloidal Movement in Asphalt." (1 reel) (Courtesy Barber Asphalt Paving Company.)

Friday, September 24

2:00 P.M.—Ceramic Symposium.
(Meeting of the American Ceramic Society, R. H. Minton, *Chairman*.)
"A Classification of Sheet Steel Enamels," R. R. Danielson, (U. S. Bureau of Standards).

8:00 P.M.—Motion Pictures: Mining Industries:
1: "The Story of Coal." (4 reels) (Courtesy Sullivan Machinery Company and U. S. Bureau of Mines.)
2: "Building, Mining, and Quarrying Machinery." (2 reels) (Courtesy Sullivan Machinery Company.)
3: "Producing Pumps and Engines." (1 reel) (Courtesy Midwest Engine Company.)
4: "Silver Mining in Ontario." (1 reel)
5: "Gold Mining in Ontario." (1 reel) (Courtesy Ontario Department of Mines.)
6: "The Manufacture of Pottery." (1 reel) (Courtesy American Ceramic Society.)

Saturday, September 25

(Speakers to be announced.)

8:00 P.M.—Motion Pictures:
1: "Manufacture of Asbestos." (1 reel)
2: "Silks and Satins." (2 reels)
(Both by Courtesy Bureau of Commercial Economics.)
3: "Foamite Firefoam Extinguishing Apparatus at Work." (1 reel) (Courtesy Foamite Firefoam Company.)
4: "Continuous Motion, Conveying, Stacking, Elevating, Loading and Unloading Machinery." (1 reel) (Courtesy Brown Portable Machinery Company.)
5: "The U. S. Ammonium Nitrate Plant No. 2 at Muscle Shoals, Alabama." (2 reels) (Courtesy Westinghouse-Church Kerr, Inc.)

EXHIBITORS

87–8	Abbé, Paul O., Inc.
77–8	Abbé Engineering Company
445–6	Acid Proof Clay Products Company
554	Ainsworth, Wm., & Son
422–3	Ajax Electrothermic Corporation
332	Alberene Stone Company
231	Alcohol Products Company
402	Allen Electrolytic Cell Corporation
241	Allis-Chalmers Manufacturing Company
201–5	American Aniline Products, Inc.
	American Ceramic Society
319–320	American Chemical and Manufacturing Company
210–210*a*	American Chemical & Sugar Machinery Company
	American Chemical Society
90	American Cyanamid Company
660	American Dressler Tunnel Kilns
741	American Dyestuff Reporter
614–6	American Dyes Institute
	American Electrochemical Society
743	American Fertilizer, The
244–5	American Hard Rubber Company
438	American Kron Scale Company
751	American La France Fire Engine Company
279–80	American Metal Company, Ltd.
404	American Metal Products Company
740	American Pulverizer Company
342	American Rolling Mill Company
715	American Steel & Wire Company
4	American Transformer Company
420	American Water Softener Company
6	Anaconda Copper Mining Company
6	Anaconda Lead Products Company
6	Anaconda Rolling Mill Department
273–4	Angel, H. Reeve, & Company, Inc.
301–4	Aniline Dyes & Chemicals, Inc.
758–9	Aniline Sales Corporation
267–8	Anti-Hydro Waterproofing Company
764–5	Anthrakone Dye Products & Chemical Company
287	Apex Chemical Company
510	Arkell Safety Bag Company
612	Armstrong Cork Company
246–7	Arnold Hoffman & Company
494	Aterite Company, Inc.
613	Atlantic Dyestuff Company
414	Atlas Electric Devices Company
735	Avery Rock Salt Mining Company
737	Babbitt, B. T.
610	Bacharach Industrial Instrument Company
336–7	Bachmeier & Company
559–61	Bailey Meter Company
333	Baker, J. T., Chemical Company
63	Baker, Joseph, Sons & Perkins Co., Inc. (Werner & Pfleiderer Div.)
82	Barber Asphalt Paving Company
18–19	Barrett Company, The
306–7	Bausch & Lomb Optical Company
77	Beach-Russ Company
732	Beaver Chemical Company
537–8	Becker, Christian, Inc.
506	Beckley Perforating Company
13	Bethlehem Foundry & Machine Company
444	Blackmer Rotary Pump Company
408	Blakiston's, P., Son & Company
462–3	Booth Electric Furnace Company
738	Boyer Oil Company, Inc.
738	Boyer Oil Manufacturing Company
84	Bristol Company, The
41	Brown Instrument Company, The
685, 692	Brown Portable Conveying Machinery Compan
253	Buckman & Pritchard, Inc.
23–27	Buffalo Foundry & Machine Company
675	Burrell Technical Supply Company
70	Calco Chemical Company
442	California Alkali Company
471	Canada Carbide Company
473	Canada: Dominion Water Power Branch
487	Canada, Iron & Steel of
491–2	Canada: Ontario Bureau of Mines
487	Canada, Pulp & Paper Magazine of
471	Canada: Shawinigan Electro Metals Company
472	Canada: Shawinigan Products Company
472	Canada: Shawinigan Water & Power Company
488	Canadian Chemical Journal
471	Canadian Electrode Company
472	Canadian Electro Products Company
487	Canadian Mining Journal
489–90	Canadian Pacific Railway
487	Canadian Textile Journal
56	Carborundum Company, The
1–2	Carrier Engineering Company
14	Celite Products Company
12	Celluloid Zapon Company
496–8	Central Scientific Company
54	Chadwick Boston Lead Company
656–7	Chapman Engineering Company
656	Chapman Stein Furnace Company
495	Chemical Age, The
29	Chemical Catalog Company, Inc.

281 2	Chemical Company of America
443	Chemical Color & Oil Daily
517	Chemical Equipment Company
42	Chemical & Metallurgical Engineering
505	Chemical Pump & Valve Company, The
308–11	Chiris, Antoine, Company
256–7	Cleveland Cliffs Iron Company
610	Cleveland Instrument Company
291	Clinchfield Products Corporation
425	Clipper Belt Lacer Company
700	Combustion
317	Commercial Solvents Corporation
522	Consolidated Chemical Products Company
432	Contact Process Company
719–20	Container Club, The
410	Color Trade Journal
338–41	Corning Glass Works
429–30	Crane Company
536	Crane Packing Company
684	Crescent Sales & Engineering Company
682	Davidson, M. T., Company
638	Davison Chemical Company
531–3	De Laval Separator Company, The
529–30	Denver Engineering Works Company
479	Dermatological Research Laboratories
468–70	Detroit Electric Furnace Company
80	Detroit Range Boiler & Steel Barrel Company
15	Devine Company, J. P.
624–5	Diamond State Fibre Company
548–9	Dings Magnetic Separator Company
473	Dominion Water Power Branch
51–2	Dorr Company, The
79	Dow Chemical Company
252	Drackett, P. W., & Sons Company
544–5	Draper Manufacturing Company
569–71	Drying Systems, Inc.
739	Dunning Lueckel Engineering Company
8, 7	Du Pont, E. I., de Nemours & Company
43	Duriron Castings Company
524–6	Eagle Picher Lead Company
631	East Jersey Pipe Company
217–21	Eastman Kodak Company
423–4	Economic Machinery Company
434–5	Economy Engineering Company
231	Edgar Bros. Company
752–3	Egyptian Lacquer Manufacturing Company, The
58	Eimer & Amend, Inc
449–50	Electric Furnace Company
321–2	Electro Bleaching Gas Company
277–8	Electrolytic Zinc Company, Inc.
401–2	Electron Chemical Company
209	Elmore, G. H
92	Elyria Enameled Products Company
344	Empire Laboratory Supply Company, Inc.
500	Engelhard, Charles
37–8	Everlasting Valve Company
732–3	Excelsior Dyestuff & Chemical Company
754–5	Falcon Dye & Chemical Company
467	Fansteel Products Company, Inc.
242–3	Fleisher & Company, W. L.
513	Florasynth Laboratories
66	Foote Mineral Company
621	Foamite Firefoam Company
346–7	Foxboro Company, The, Inc.
609	Fuel Products Corporation, The
284–5	Garrigue, Wm., & Company
716–7	Garrigues, Chas. F., Company
712–4	Geigy Company, Inc
3	General Bakelite Company
742	General Briquetting Company
2, 222–4	General Ceramics Company
17–18	General Chemical Company
5	General Electric Company
427	General Electric Company (Lake Erie Chemical Works)
251	General Filtration Company, Inc.
227	General Fire Extinguisher Company
54	Georgia Lead Works
54	Gibson & Price Company
508–9, 523	Glamorgan Pipe & Foundry Company
678–9	Glass Coating Company
32	Glens Falls Machine Works
228–30	Gordon Dryer Corporation
711	Gottesman, M., & Company, Inc.

47	Goulds Manufacturing Company
772–3	Greeley Products Corporation
215–6	Greiner Company, Emil
50	Groch Centrifugal Flotation, Ltd.
88	Gruendler Patent Crusher & Pulverizer Company
694	Guernseyware Company
451–2	Hamilton & Hansell, Inc.
499–500	Hanovia Chemical & Manufacturing Company
60	Hardinge Company
703	Hauser-Stander Tank Company
250	Haynes Stellite Company
441	Hays, Jos. W., Corporation
751	Hayward, S. F., & Company
35–6	Hepworth, S. S., Company
680, 681, 696, 697, 71	Hercules Engineering Corporation
323–5	Hercules Powder Company
226	Herold China & Pottery Company
636	Heyden Chemical Company, of America
701	Heyl Laboratories
10–11	Hooker Electrochemical Company
296–7	Hoskins Manufacturing Company
54	Hoyt Metal Company
44	Huff Electrostatic Separator Company
493	Hunter Dry Kiln Company
567	Huyck, F. C., & Sons
736	Hydrocarbon Chemical Company
641	Imperial Dyewood Corporation
565–6	Independent Chemical Company
487	Industrial & Educational Press
454–5	Industrial Electric Furnace Company
67	Industrial Filtration Corporation
745–6	Innis Speiden & Company, Inc.
44	International Carbon Products Company
456–8	International Nickel Company
735	International Salt Company
487	Iron & Steel of Canada
440	Irving Iron Works Company
766–7	Jacques Wolf & Company
428	Jewell Polar Company
635	Joplin Whiting Company
A (Mezz Fl.)	Journal of Commerce, The
29	Journal of Industrial & Engineering Chemistry
555–6	Kalbfleisch Corporation, The
405–6	Kenart Synthetic Products Company
497	Kewaunee Manufacturing Company
565	King Chemical Company
617–9	Klipstein, A., & Company
484–6	Knight, Maurice A.
326–1	Knoxville Board of Commerce
312–3	Koppers Company, The
313	Koppers Products Company
427	Lake Erie Chemical Works of General Electric Company
667, 674	Lakewood Engineering Company
756–7	Lamie Chemical Company, Inc.
345	Lammert & Mann
733	Laurel Soap Manufacturing Company
465	Lead Lined Iron Pipe Company
55	Leeds & Northrup Company, The
627	Liberty By-Products Company
520–1	Lindsay Light Company
403	Liquid Carbonic Company, The
633	Loomis-Manning Filter Distributing Company
283	Lungmotor Company, The
260–1	Lunkenheimer Company, The
734	Luzerne Rubber Company
620	Maas & Waldstein Company
658	Magnesia Association of America
421–2	Magnetic Manufacturing Company
433	Mann & Cook
318	Manufacturers Record
206 8	Mathieson Alkali Works, Inc
87	Mead & Company
89	Merck & Company
213–4	Merrill Company, The
277 8	Metals Disintegrating Company
525	Midland Chemical Company
550–1	Mid-West Engine Company
675	Mine Safety Appliance Company
59	Mine & Smelter Supply Company
9	Mineral Point Zinc Company
231	Miner-Edgar Company
677	Mojonnier Bros. Company

412	Monarch Manufacturing Works, Inc.
457	Monel Metal Products Company
661	Mono Corporation of America
611	Morse Chain Company
75	Mott, J. L., Iron Works
254–5	Multi-Metal Company, Inc.
629	Mobile & Ohio Railroad
91	Nash Engineering Company
634	Nassau Valve & Pump Corporation
20–22	National Aniline & Chemical Company
718	National Binding Machine Company
518	National Filter Cloth & Weaving Company
28	National Gum & Mica Company
427	National Lamp Works of General Electric Company
739	Nelson, Alfred W.
298–9	Newark Wire Cloth Company
639	New England Tank & Tower Company
8, 9	New Jersey Zinc Company
62	Newport Chemical Works, Inc.
626–8	New York Color & Chemical Company
729	New York Container Company, Inc.
314–5	Niagara Alkali Company
265	Niagara Electrochemical Company
622–3	Nichols Copper Company
666	Nitro Products Company
207	Nitrogen Corporation
34	Norton Company
683	Northwestern Chemical Company
466	Obermayer, S., Company, The
286	Oil, Paint & Drug Reporter
269–70	Oliver Continuous Filter Company
491–2	Ontario Bureau of Mines
294–5	Organic Salt & Acid Company
439	Oxygen Products Company
515–6	Ozone Company of America
93	Palo Company, The
695	Paper Mill & Wood Pulp News
552–3	Parks-Cramer Company
441	Payne, Stephen H.
33	Pennsylvania Salt Manufacturing Company
480–1	Permutit Company, The
264	Perth Amboy Chemical Works
568	Perry & Webster, Inc.
519	Peterson, Leonard & Company
73	Pfandler Company
289–90	Philadelphia Drying Machinery Company
501	Philadelphia Quartz Company
474	Pittsburgh-Des Moines Steel Company
415–7	Pneumercator Company
730	Pneumatic Scale Corporation, Ltd.
698–9	Power Specialty Company
659	Powers Regulator Company
744	Powhatan Mining Company
541–3	Pratt Engineering & Machine Company
80	Precision Instrument Company
702	Protecto Safety Appliance Company
640	Procter & Gamble Distributing Company
233–6	Proctor & Schwartz
78	Provost Engineering Corporation
487	Pulp & Paper Magazine of Canada
288	Pyroelectric Instrument Company
539–40	Quigley Furnace Specialties Company, Inc.
665	Raritan Aniline Works
6	Raritan Copper Works
49	Raymond Brothers Impact Pulverizer Company
54	Raymond Lead Works
464	Refinite Company
512	Republic Flow Meters Company
4	Research Corporation
258–9	Revolvator Company, The
760–1	Rhodia Chemical Company
12	Richards Company
54	Robertson, Jas., Lead Works
426	Robinson, Dwight P., & Company, Inc.
264–6	Roessler & Hasslacher Chemical Company
292–3	Rollin Chemical Corporation
441	Roto Company, The
83	Ruggles Coles Engineering Company
504	Sarco Company
502–3	Schaar & Company
65	Schaeffer & Budenberg Manufacturing Company
431	Schwartz Sectional System
498	Scientific Equipment Company
316	Scott & Company, Ernest
731	Scott & Company, Henry L.
16	Semet-Solvay Company
271–2	Seydel Manufacturing Company, The
507	Seymour & Peck Company
94	Sharples Specialty Company
472	Shawinigan Electrometals Company
471	Shawinigan Products Company
471–2	Shawinigan Water & Power Company
48	Sherwin-Williams Company, The
39	Sidio Company of America
693	Simmons, John, Company
709–10	Sly, W. W., Manufacturing Company
413	Soderling, Walter, Inc.
16	Solvay Process Company
632	Southern Cotton Oil Company
772	Southern Oil & Chemical Company
629–30	Southern Railway System
72	Sowers Manufacturing Company
534–5	Sparks, John C.
627	Stamford Dyewood Company
566	Stauffer Chemical Company
211–2	Stein Hall & Company, Inc.
565	Sterling Color Company
610	Sticht, Herman H., & Company
557–8	Stimpson Equipment Company
85–6	Stokes, F. J., Machine Company
30–1	Sturtevant Mill Company
459–60	Sullivan Machinery Company
562–4	Sunbeam Chemical Company
64	Swenson Evaporator Company
475	Taber Pump Company
275–6	Tagliabue, C. J., Manufacturing Company
763	Takamine Commercial Corporation
762–3	Takamine Laboratory, Inc.
762	Tanner, Chas. S., Company
248–9	Taylor Instrument Companies
747–8	Texas Gulf Sulphur Company
514	Textile Colorist
511	Textile World Journal
637	Textiles
666	Thatcher Products Company
57	Thermal Syndicate, Ltd., The
232–3	Thermo Electric Instrument Company
527–8	Thomas, Arthur H., Company
40	Thwing Instrument Company
262–3	Titanium Alloy Manufacturing Company
263	Titanium Pigment Company
68–9	Tolhurst Machine Works
721, 728	Tyler, W. S., Company, The
45	Uehling Instrument Company
665	Uniform Chemical Products Company
237–40	Union Steam Pump Company
418	Union Sulphur Company
53	United Filters Corporation
54	United Lead Company
54	United Lead Company—Tatham Brothers Works
54	United Lead Company of Cincinnati
54	United Lined Tube & Valve Company
6	United Metals Selling Company
76	United States Cast Iron Pipe & Foundry Company
300, 305	U. S. Industrial Alcohol Company
305	U. S. Industrial Chemical Company
461	U. S. Smelting Furnace Company
733	Universal Dyes & Chemical Company
738	Universal Oil Company
436–7	Valley Iron Works
419	Van Nostrand, D., Company
664–6	Van Winckel, W. H.
343	Vitreous Enameling Company
566	Vulcan Detinning Company
676	Wailes Dove-Hermiston Corporation
225	Wallace & Tiernan Company, Inc.
768–70	Warner Chemical Company
33	Wedge Mechanical Furnace Works
63	Werner & Pfleiderer Company
426	Westinghouse-Church Kerr, Inc.
46	Westinghouse Electric & Manufacturing Company
654–5	Wheeler, C. H., Manufacturing Company
334–5	Whitall Tatum Company
411	Whitlock Coil Pipe Company, The
407	Widney Test Laboratories
546–7	Worthington Pump & Machinery Corporation
12	Zapon Leather Cloth Company
61	Zaremba Company

REPORT OF THE COMMITTEE ON LEGISLATION OF THE AMERICAN DYES INSTITUTE

At the meeting of the American Dyes Institute held at the Hotel Griswold, Eastern Point, New London, Conn., July 15, 1920, the Institute's Committee on Legislation presented an interesting review of the efforts to secure from Congress legislation adequately protecting the American dye industry.

The report outlines the progress of the legislation in the House, through hearings held by the Ways and Means Committee. It records the passage of legislation by the House, and then deals with its consideration, through hearings by the Senate Finance Committee, where a qualified embargo plan was substituted for the license plan of the House bill, and in this form unanimously reported to the Senate.

Immediately upon the report of the bill it became the object of persistent criticism and attack from its opponents.

It would be useless at this time to review in detail the objections urged by the opponents of the Senate bill. Your Committee and its counsel were constantly available to analyze from both the manufacturing and legal viewpoint the numerous proposals to amend the bill. Save in a few instances, the opposition to the legislation was from the importers who obviously wanted the fullest possible chance to import foreign dyes with which to undersell the American producer, or from that minority of consumers more concerned with an immediate competitive market in dyes than with the establishment of a thoroughly independent and self-sustaining dye industry in the United States. It is fair to say in this connection that there were a few instances where constructive suggestions for changes came from consumers who are in sympathy with the proposed legislation.

Your Committee, in presenting the case for the American dyes industry to the committees of the House of Representatives and the Senate, proceeded upon the openly declared idea that the testimony of impartial witnesses at the hearings would abundantly establish the fact that an American dye and related coal-tar chemical industry is absolutely essential to the national defense and national welfare, and that the existence of high tariff duties on foreign dyes and intermediates is not by any means enough to protect such an industry in the United States from destruction through foreign commercial attack during the temporary period when it is developing complete production for the country. In other words, your Committee proceeded upon the frank theory that a practical embargo against foreign dyes of the same kind and quality as those being produced commercially in the United States is a conceded necessity until our industry is fully developed.

You are familiar with the testimony at the hearings, and, of course, know that it was established by the statements of military experts and chemists who have no connection with the dye manufacturers that a complete and self-sustaining dye and coal-tar chemical industry in the United States is a vital necessity for our national defense, national health, and general industrial welfare. The completeness with which that truth was brought out is, we are entitled to believe, evidenced by the passage of the bill in the House of Representatives by a substantial majority, and by the favorable report of the amended Senate bill by the Finance Committee.

Notwithstanding the pressure of legislative business in the Senate and the pendency of the peace treaty as a continual problem, the Senate by a very substantial majority vote took up the dyes bill for consideration with a view to its passage. With the urgent necessity for providing the necessary appropriations to operate the Government for the current fiscal year supplementing the peace treaty situation, those opposed to the legislation in the form in which it was reported by the Senate Committee were able to occupy a sufficient amount of time of the Senate, under existing rules, to make those in charge of the bill appreciate the impossibility of attempting to press the measure for passage.

At the same time, your Committee is glad to be able to report that apparently a decided majority of the members of the Senate favor the passage of legislation to protect the American dye industry on the general plan embodied in the pending bill. The essential character of the industry as related to the national defense and national health seems to have been generally accepted, the vote for consideration above referred to clearly justifying such assertion by your Committee.

* * * * *

The great majority of the dye consumers of the country have been vigorously supporting the proposed legislation. These consumers have appreciated that both in the original "license system" proposed by the manufacturers and adopted by the House, and in the "qualified embargo" plan substituted by the Senate committee, adequate provision was made for the consumers to secure from time to time all varieties of foreign dyes when the same kind or satisfactory substitutes are not made in this country.

The attitude of your Committee has been, and in that it knows it has expressed the view of the dye industry, that the consumer must be given ample opportunity to have as full a variety of colors as the consumers of other countries. Coöperation between the manufacturer and the consumer is essential in the dye industry, and it is the Committee's view that a continuance of the recent coöperation may be looked for from the consumers who have heretofore supported the legislation necessary to develop our industry.

* * * * *

The adjournment of Congress on June 5 last did not operate to defeat the pending bill. It retains its status as a bill passed by the House of Representatives, reported with amendments by the Senate Finance Committee, and on the Senate calendar for consideration. In other words, it may be called up for final passage in the Senate at any time in the session of Congress beginning on the first Monday of December next.

In the meantime it is, of course, known that the Congress provided an appropriation for the War Trade Board Section of the Department of State so that the dye consumers may import their necessary six months' supplies of dyes not yet made in the country, while at the same time the general importation of foreign dyes to injure or destroy the American producers may be effectively prevented.

AMERICAN CERAMIC SOCIETY AND BRITISH SOCIETY OF GLASS TECHNOLOGISTS

A joint meeting of the glass division of the American Ceramic Society and British Society of Glass Technology will be held in Pittsburgh, Pa., September 1 to 3, 1920.

Dr. W. E. S. Turner, of the University, Sheffield, England, and about forty members of the British Society of Glass Technology, arrived in New York on August 20 for an industrial visit to American glass plants. They will be in Pittsburgh from August 28 to September 6, and will be entertained by the Glass Division of the American Ceramic Society. Dr. E. Ward Tillotson, of Mellon Institute, Pittsburgh, Pa., is secretary of the committee on arrangements.

CHEMICAL WARFARE POST OF THE AMERICAN LEGION

The Chemical Warfare Post of the American Legion will hold its next meeting at 8 P.M., September 22, 1920, in the conference room of the Grand Central Palace, Lexington Avenue and 45th Street, New York, N. Y.

At that time a permanent organization will be effected. Membership in the Post is open to all C. W. S. ex-service men. Application for membership, which must be accompanied by payment of dues, should be sent to the treasurer, Dr. F. G. Zinsser, Hastings-on-Hudson, N. Y. For members entering the Legion that fee is \$3.50. If you are already a member but wish to enroll in our Post as well, the fee is \$2.00.

The Chemical Warfare Post is established as a means towards rendering unselfish service to the nation. It recognizes no past distinctions of rank. It plans to place its affairs in the hands of those who can think clearly, see well, and fight hard. With your aid success can be reached.

NEW YORK, N. Y.
August 16, 1920

LESLIE T. SUTHERLAND, *President*

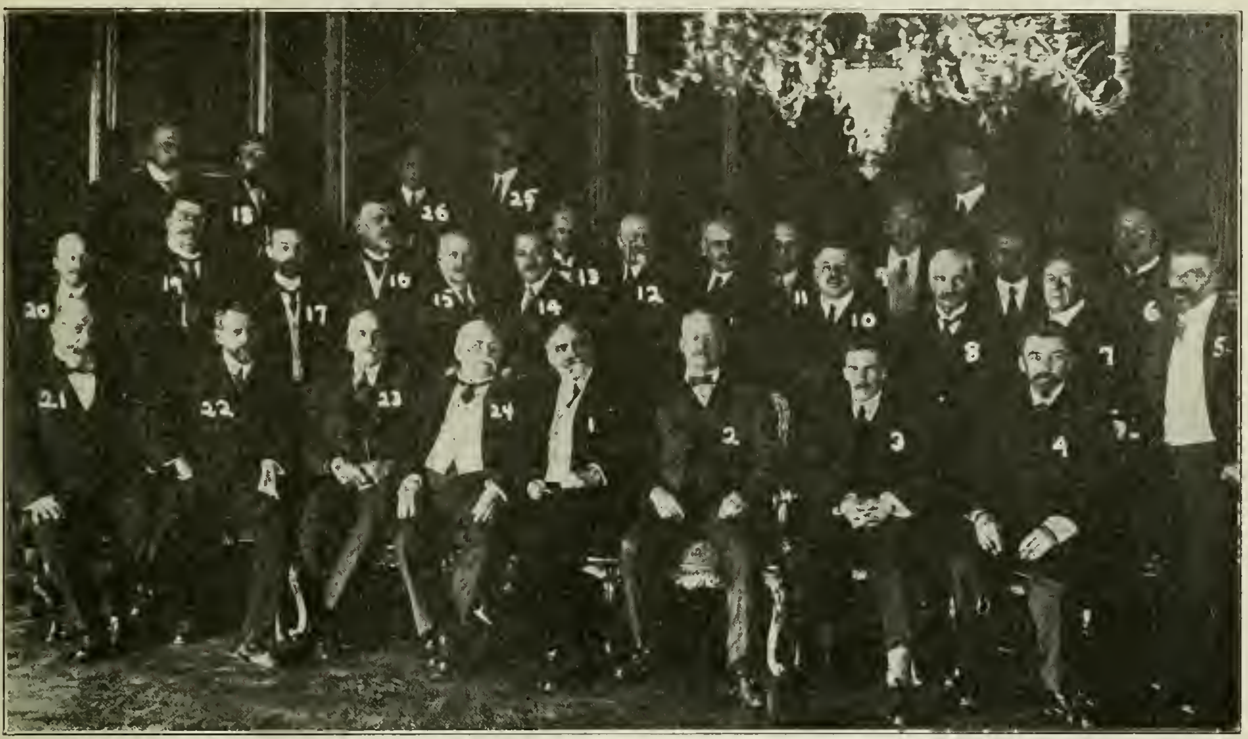
CALENDAR OF MEETINGS

American Chemical Society—Sixtieth (Annual) Meeting, Congress Hotel, Chicago, Ill., September 6 to 10, 1920.

Sixth National Exposition of Chemical Industries—Grand Central Palace, New York, N. Y., September 20 to 25, 1920.

American Electrochemical Society—Fall Meeting, Hotel Statler, Cleveland, Ohio, September 30 to October 2, 1920.

THE INTERNATIONAL CHEMICAL CONFERENCE



1—Moureu, 2—Parsons, 3—Hay, 4—Swarts, 5—Lucion, 6—Biilmann, 7—Garelli, 8—Ciamician, 9—Kruyt, 10—Lormand, 11—Gerard, 12—Matignon, 13—Kestner, 14—Nicolardot, 15—Kowalski, 16—Bordas, 17—Bertrand, 18—Marie, 19—Quartieri, 20—Zenghelis, 21—Nasini, 22—Votocek, 23—Lindet, 24—Paterno, 25—Marotta, 26—Crespi

By Charles Lormand, 4, Avenue de l'Observatoire, Paris, France

The third session of the International Chemical Conference met at Rome, June 21 to 25, with Professor Charles Moureu, member of the Institute of France, as president.

The program began with the meeting of the Council of the International Union of Pure and Applied Chemistry, composed of the representatives of the five nations which founded the Union. The Council considered the adhesion to the Union of seven new countries: namely, Canada, Denmark, Spain, Greece, the Netherlands, Portugal, and Czecho-Slovakia, which were all admitted.

The General Assembly was then organized, consisting of the following delegates: *Belgium:* Prof. Frédéric Swartz of the University of Gand, member of the Royal Academy of Belgium; Dr. René Lucion, past president of the Société Chimique de Belgique, head of the laboratory at the Société Solvay. *Denmark:* Dr. Einar Biilmann, professor of chemistry at the University of Copenhagen, president of the Danske Kemiscke Foreningers Faellesraad for Internationalt Samarbejde; Mr. Warming, engineer-in-chief of A/S Dansk Svovlsyre og Superphosfabrik. *United States:* Dr. Charles L. Parsons, secretary of the American Chemical Society. *France:* M. G. Bertrand, president of the Société Chimique de France, professor at the Faculté des Sciences de Paris, chief of the Institut Pasteur; M. F. Bordas, assistant professor at the Collège de France, director of the laboratories of the Ministry of Finance; M. Jean Gerard, chemical engineer, secretary general of the International Union of Chemistry, and of the Fédération Nationale des Associations de Chimie de France; M. Paul Kestner, president of the Société de Chimie Industrielle; M. L. Lindet, member of the Institut, member of the Accademia Nazionale dei Lincei, president of the Association des Chimistes de Sucrerie et de Distillerie, professor at the Institut Agronomique; M. Ch. Lormand, chemist at the laboratory of the Ministry of Agriculture, member executive committee of *Chimie et Industrie;* M. Camille Matignon, vice president of the Société de Chimie Industrielle, professor at the Collège de France; M. Ch. Marie, secretary of the Société de Chimie Physique, and of the International Committee of Tables of Constants; M. Ch. Moureu, member of the Institut, president of the International Union of Chemistry and of the Fédération Nationale des Associations de Chimie, professor at the Collège de France; M. Nicolardot, examiner for admission and private tutor at the École Polytechnique. *Great Britain:* Sir William Pope, president of the British Federal Council for Pure and Applied Chemistry, and of the Society of Chemical Industry, professor at Cambridge University; Mr. Hay, chemical engineer, technical delegate to the Reparation Commission. *Greece:* Prof. Zenghelis, of the University of Athens. *Italy:* Prof. G. Bruni, of the Polytechnique at Milan; Prof. G. Ciamician, of the University of Bologna, president of the Associazione Italiana di Chimica Generale ed Applicata; Prof. F. Garelli, of the Polytechnique at Turin; Prof. R. Nasini, of the University of Pisa, member of the Conseil Supérieur de l'Instruction Publique; Ing. L. Parodi-Delfino, vice president of the Associazione Italiana di Chimica Generale ed Applicata; Prof. G. Oddo, of the University of Palerma; Prof. Plancher, of the University of Parma; Dr. E. Paterno, president of the Consiglio Nazionale di Chimica, professor at the University of Rome, member of the Accademia Nazionale dei Lincei, member of the Conseil Supérieur de la Santé Publique; Ing. F. Quartieri, director of the Società Italiana Prodotti Esplodenti; Prof. A. Peratoner, of the University of Rome. *Netherlands:* Dr. R. H. Kruyt, professor of physical chemistry at the University of Utrecht, president of the Nederlandsche Chemische Vereeniging. *Poland:* Prof. Kowalski, of the Polytechnic School of Warsaw. *Czecho-Slovakia:* Dr. E. Votocek, professor of general, mineralogical, and organic chemistry at the Polytechnic School at Prague, president of the Chemical Society of Bohemia.

The meetings were held at the headquarters of the Accademia Nazionale dei Lincei, the Corsini Palace, one of the most beautiful in Rome. The meetings were presided over in turn by one of the visiting delegates. Reports on the questions included in the program were presented to the assembly by committees which had been appointed to give them preliminary consideration and to make recommendations.

ORGANIZATION AND ADMINISTRATION OF THE UNION

The plan of organization and administration of the International Union of Pure and Applied Chemistry, which was presented by M. Gerard, was as follows:

To adhere to the Union a country must establish a liaison between its chemical groups by the formation of a national council or federation. The initiative of this organization must be taken by a chemical society, the National Academy, the National Research Council or a similar national institution, or by the government.

The Union is governed by the Council, composed of delegates from each of the supporting countries, whose executive power is vested in a Bureau. The General Assembly receives reports from the Council, approves the accounts of the past session, adopts the budget for the following session, and considers the questions to be included on the program. Under the Council and an Executive Committee, a permanent staff carries out the program of action as defined by the Bureau. This staff is situated at the headquarters of the Union, and is the pivot of all the organizations connected therewith. The Council can also establish permanent committees as they may seem necessary.

An Advisory Committee, divided into sections corresponding to the different scientific and industrial branches, considers in detail the questions figuring in the program of action. The associated nations are represented in each section by delegates, elected for three years. The delegates of each nation constitute a National Committee, whose duties include the study of questions interesting to chemistry from scientific, industrial, and economic points of view.

A meeting of the Council, of the permanent committees, of the Advisory Committee, and of the General Assembly is held each year, under the title of the "International Chemical Conference."

The report presented by Professor Lindet, for the Fédération Nationale des Associations de Chimie de France, asking that the International Congress be joined to the Union, provides that the International Conference shall every four years be converted into an International Congress of Pure and Applied Chemistry. Elections to the Council, to permanent committees, and to the Advisory Committee shall take place at this time.

The languages for the Congress are English, French, and Italian. Communications may be made in another language, provided authors give a translation or an abstract in the official languages. To avoid errors in interpretation, communications, votes, resolutions, and official acts, if not originally offered in French, must be translated into that tongue.

To encourage research, the Council may, within the limit of funds granted each year by the Assembly, award prizes and medals to the authors of work considered worthy of such distinction.

COMMITTEE REPORTS

UNIFICATION OF ANALYSIS—Passing to the report of M. Nicolardot on the unification of chemical analysis, the Conference voted that the international agreement signed at Paris on October 16, 1912, for unification of the presentation of analytical results on food materials, and for the creation in Paris of a permanent international bureau dealing with these matters, be ratified and put in operation as soon as possible.

CHEMICAL STANDARDS—In connection with the report of M. Crismer on an international institute of chemical standards, the Conference ordered the Council to organize a bureau divided into three sections: chemical standards, pure products for research, and technical products.

The Bureau of the Union will provide for the transfer of products from scientists, manufacturers, and dealers to the sections interested.

The United States will organize a branch related to the Union in the same way as the other Sections, which will be responsible for carrying out the conditions fixed by the donors. Three Sections shall be organized, by Belgium, Great Britain, and France.

In consideration of the importance of the thermochemical contributions, a special subcommittee urged the appointment of a committee to prepare a tentative plan for the establishment of standards from the thermochemical standpoint.

PATENTS—The report on the determination of the legal value of sealed applications for patents caused debate which ended in the following vote: The International Union of Pure and Applied Chemistry will organize a group of men competent from the technological and judicial point of view to study questions relative to patents. Italy has been charged with preparing a plan of organization. The Conference considers the first questions to be the legal value of sealed applications and the creation of international patents.

ATOMIC WEIGHTS—The examination of the report of Mr. W. D. Bancroft, chairman of the Division of Chemistry and Chemical Technology, led the Union to establish an International Committee on Atomic Weights. Messrs. Thorpe, Clarke, and Urbain, members of the old committee, were requested to continue this work.

It was decided to inscribe on the order of the day of the next Congress the two following proposals: that the revision of the table of atomic weights be decennial, in order to give time to check the latest determinations; and that the proposal of Dalton, of assuming $H = 1$ as the basis of the system, be re-adopted.

TABLES OF CONSTANTS—At the suggestion of M. Charles Marie, the Conference decided to connect with the Union the International Committee on Tables of Constants. Its secretary will present each year to the Union a report on the work of the Committee, which, after approval, will be transmitted to the International Research Council for final approval.

PHYSICOCHEMICAL SYMBOLS—In regard to physicochemical symbols, the Conference, at the request of the Chemical Society, will ask chemical associations and chemical journals of the adhering countries to republish the list approved by the old International Association of Chemical Societies at their last meeting at Brussels, September 23, 1913.

To draw the attention of the respective governments to the importance of the work of the Union, the following resolution was adopted: The Conference of the International Union of Chemistry resolves that all the delegates of the nations belonging to the Union are trying to make known the public value of the work of the Union.

The Bureau will send to the Italian government a verbatim report of the Conference with the request that it be officially transmitted to the governments of the other countries.

The Conference decided to hold its next meeting at Warsaw in 1921.

ENTERTAINMENT OF DELEGATES

Perfect arrangements for the meeting had been made by Professor Marotta, secretary of the "Consignio Nazionale di Chimica." This society rendered the stay of the delegates in Rome as agreeable as it was profitable. Special tickets permitted them to visit the museums, monuments, and wonders of the Eternal City. Brilliant receptions and banquets were offered. The Syndic of Rome personally received the members of the Conference.

The Naples Section of the Associazione Italiana di Chimica Generale ed Applicata had arranged an excursion to Pompeii to the new excavations.

The Italian manufacturers in their turn showed that their country, without ceasing to be the fatherland of art, is also capable of the industrial effort which modern society demands. The delegates were invited to visit three important Italian factories which the war brought into being and which are now being transformed for the work of peace, those of Bombrini Parodi-Delfino at Segni, Electro-Chimica Pomilio at Naples, and Prodotti Esplodenti at Cengio. Messrs. Parodi-Delfino, Pomilio, and Quartieri, the pioneers of Italian industry, and their colleagues, showered the delegates with information as to the results obtained in their factories, from the point of view of organization and of productivity. The banquets which they gave were the occasion for expressions of thanks, on the part of the heads of the delegations, to Italy for the cordiality of their reception.

The work of the International Union in the course of this Conference has one special value. It forms the basis of a permanent organization, the advantages of which will be felt in every country.

WASHINGTON LETTER

By J. B. McDonnell, Union Trust Building, Washington, D. C.

In anticipation of a revision of the tariff when the new Congress, which is to be elected this fall, comes in, the United States Tariff Commission is bending its efforts to complete the gathering of data on all American industries.

Schedule A of the tariff law deals with chemicals, and the Commission experts expect to have their data upon these industries completed and ready for submission to Congress sometime before the new Congress meets for the first time next March.

General revision of the tariff during the session beginning with March is very improbable, although some small beginning may be made along that line.

CHARACTER OF OPPOSITION TO DYE LEGISLATION

Aside from the general revision of the tariff, however, there are pending before the Senate several measures of keen importance to the chemical world. Not the least of these is the dye bill, and on its account election of the new Congress is of great interest to the chemists of the country, particularly as regards some of the pre-election campaigns being waged by members of the Senate. Several senators who took a more or less prominent part in the fight on the dye bill are experiencing the battles of their political careers in their efforts to obtain the nomination of their respective parties. Some of the opponents of the dye bill will bid the Senate adieu with the expiration of their present terms. This cannot be expected to cause any great regret in quarters interested in development of an American chemical industry which is of such paramount importance to the commerce and defense of the nation.

Opposition of some of these Senators was undoubtedly the expression of their honest convictions; of others it was the anxiety to protect, as Senator Moses of New Hampshire expressed it, the interests of their "clients." "Clients" was a favorite expression of Senator Moses in discussing his opposition to the dye bill. Opposition of his "clients" to a measure is rather a peculiar explanation for a member of the United States Senate to give for his efforts to defeat a measure so important to the national defense.

News comes from Colorado that Senator Thomas, Democrat, has lost out in his fight to obtain the nomination from his party for another term. Senator Thomas, it will be remembered, distinguished himself during the closing days of the last session by taking a large part in the actual filibuster that delayed action on the dye bill. The honesty of his opposition, however, will be conceded much more quickly than in the case of others.

From New Hampshire come stories of another primary fight of particular interest to the chemists, and to the country as a whole. Senator Moses is in danger of losing the primary fight. He it was who was responsible for the defeat of efforts to pass the dye bill. Those who were in intimate touch with the dye fight do not give credit to the New Hampshire Senator for the same honesty of purpose that they give to others.

"Clients" and "Amoskeag" were too often used by Senator Moses to leave any doubt as to the cause of his bitter efforts to defeat legislation designed to build up an industry that should stand as a bulwark between our country and enemy nations. It is hardly to be expected that New Hampshire will again send a man to the Senate who will so easily assume the yoke of the Amoskeag corporation and do its bidding. Senator Moses may be in a difficult position if he is reëlected. The Atlantic Dyestuffs Company has purchased the government shipyards at Portsmouth and intends to erect a large plant there. Those inclined toward betting, however, can safely place their money on Senator Moses' standing by the Amoskeag, one of the bitterest opponents of an American dye industry.

Just what an American dye industry means to the ordinary person can best be told by the mothers, wives, and sweethearts of those immortal hero Americans who fell victims to the creeping, hideous gases which shriveled their very souls before it killed. These gases were the product of the German dye factories. Against the German chemical industry the only protection is a greater American industry.

There were enough votes to pass the dye bill at all times. The support was absolutely non-partisan. Without the cloak-room lobbying and misrepresentation to other members of the Senate, pursued by Senator Moses, the opposition would not have lasted. It is to this protector of his "client's" interests the public should turn to give their thanks for failure of this measure for their protection to pass the Senate.

Senator Moses introduced two amendments to the bill, ostensibly to protect the textile interests of his state. His amendments were intended to emasculate the measure; to rob it of its protecting features, and give German dyes a free gateway into the United States and a foothold toward another world monopoly. The first of these is said to have come from the Amoskeag Company, with which the Senator kept in very close touch during the fight. Mr. Dumaine, treasurer of the company, made frequent trips to Washington to see Senator Moses during the fight and made the senator's office in the Capitol his headquarters while here.

Harry S. Knight, of the law firm of Knight & Taggart, of Sunbury, Pa., drew the second Moses amendment. Mr. Knight was in Washington often, and he too made his headquarters in Senator Moses' office. He attended a private meeting of the Senate Finance Committee, and submitted a brief in which he attempted to defend his so-called amendment and answer the criticisms of the United States Tariff Commission, which said that the amendment was unworkable. Mr. Knight said he represented the Sunbury Converting Works, which are owned by the Susquehanna Silk Company. The Alien Property Custodian now holds \$2,500,000 of the preferred stock of this company because of German ownership. Many of the employees of the concern were born in Germany and reports on file at the Department of Justice here say that, during the time American soldiers were dying before the gases of the German dye factories, these employees retained their allegiance to Germany and held secret meetings with the object of helping the Fatherland. The stock held by the Alien Property Custodian is said to be owned by H. E. Schniewind, a firm at Elberfeld, Germany.

Messrs. Moses, Knight, and Dumaine held many conferences on the dye bill here. Whether Senator Moses was concerned solely for the American textile industry can be answered with the statement that large textile concerns in his own state, with the exception of the Amoskeag corporation, supported the dye bill, as did other prominent textile men throughout the country. It cannot but be hoped that some one not so closely allied to the Amoskeag will be sent by New Hampshire to represent her in the Senate, rather than he who at present occupies the place.

It might be interesting to quote a paragraph from the speech in support of the dye bill delivered in the Senate by Senator Nugent of Idaho, Democrat. After reviewing the increased cost of goods and the reasons for these increases advanced by manufacturers, Senator Nugent continues:

> How one big manufacturer has "suffered" by these adverse conditions is shown by the accounts of the Amoskeag Manufacturing Co. Not only has it shifted the burden of higher taxes, wage increases, etc., to the consumer through the medium of increased prices, but it has, at the same time and through the same medium, been able to swell its profits in a manner that is not short of being sensational.

He was quoting from an article printed in the *Evening World* of New York. It is interesting to point out that this "client" of Senator Moses prospered greatly under the far-famed Schedule K of the tariff law which aroused so much adverse criticism.

TARIFF COMMISSION REPORTS

Reports which are under preparation by experts of the Tariff Commission, and which probably will be published about the middle of September, include one on the barium chemical industries, and another on the crude botanical drug industry. These reports are numbered Tariff Information Series 18 and 19, respectively.

C. R. DeLong is preparing the report which discusses the relation of barytes, the raw material, to the barium chemical and lithopone industries. It points out the dependence of the domestic lithopone industry, prior to the war, upon the imports of German barytes, and the effect of the lithopone industry on the development of southern deposits of barytes in Georgia and Tennessee.

Production of barytes in this country at the present time is about two and a half times the pre-war imports. Before the war it was restricted to Missouri deposits, and the Atlantic market was supplied by imports from Germany. Naturally, the lithopone industry was located along the Atlantic coast, but with the development of American sources of raw material it has now branched out, and plants have been established in Chicago and St. Louis.

The report contains a chapter giving detailed costs of mining crude barytes and of manufacturing ground varieties, barium chemicals, and lithopone. Study of the freight rates from the chief producing centers of barytes to the chief consuming markets also is included. The report, of course, offers no suggestions as to the protection of the American industry, but it shows that if Congress is to protect it the duty on barytes must be at least doubled.

Professor E. E. Stanford and S. D. Kirkpatrick, the latter attached to the staff of the Commission as one of its chemical experts, have collaborated on the report on the crude botanical drug industry, which discusses foreign and domestic articles of chief importance to the drug trade, with special emphasis upon their production and consumption in relation to the tariff. There also is included a review of the tariff policy in relation to drugs. This makes the first time drugs have been considered in a government publication from the tariff point of view.

Certain articles, such as belladonna, digitalis, and wormseed, or santonia, are now grown on considerable scale in the United States, and will probably figure conspicuously in tariff revision when Congress turns its attention to that subject. Others, such as opium, cocaine, cinchona bark, and quinine, have been an important source of revenue in the past, and, because of the fact that they cannot be grown successfully in this country, will continue to be imported.

While the forthcoming census of dyes and coal-tar chemicals, now under preparation by the Tariff Commission, is expected to show many interesting developments, such as growth in total production, and greater variety of products with many new colors, collection of statistics has not yet reached the stage where any definite conclusions can be drawn. A. R. Willis, who is in charge of the census, has not yet begun any analysis of the figures which he has received. This delay can be attributed to the difficulty of collecting statistics through the field force of the bureau of the census of manufactures of the Commerce Department. The report is expected to be ready in about a month and a half, although a very large number of the principal schedules upon which it is based are still to come from the bureau of the census.

BUREAU OF MINES REPORTS

Reports of investigations into talc and soapstones, conducted by Raymond B. Ladoo, and a motor gasoline survey, by N. A. C. Smith, petroleum chemist of the Bureau of Mines, have recently been made public by the Bureau. The second semiannual survey of the motor-gasoline industry has just been completed and the analytical results apparently show "that there has been a greater decrease in the volatility of motor gasoline than can be accounted for as the normal change from winter to summer quality," as Mr. Smith declares in his report.

Investigation of the fundamentals of oil-shale retorting also is the subject of a Bureau of Mines report, prepared by Martin J. Gavin, refinery engineer of the Bureau, and Leslie H. Sharp, chemical engineer of Colorado.

OFFICE OF DEVELOPMENT WORK, BUREAU OF CHEMISTRY

Establishment of an Office of Development Work in the Bureau of Chemistry of the Department of Agriculture has been announced. The staff of the new service will be made up of engineers rather than chemists, and David J. Price, chief engineer in the dust-explosion investigations conducted by the department, will be in charge. The purpose of the new office is to assist commercial and industrial concerns to apply new processes and discoveries of the chemists in the Department. Its establishment was urged upon Secretary of Agriculture Meredith by Dr. Carl L. Alsberg, chief of the Bureau of Chemistry, who declared that it was "urgently needed to translate the work of the Bureau into terms that could be understood and applied by the manufacturer and investor." Data upon the supply of raw material, cost of production, and uses to which the product is adapted will be furnished by the development work office.

THE GERMAN DYE SITUATION

Present-day conditions in the German dye and chemical industries have been more or less accurately described in recent published reports, according to Dr. Charles L. Parsons, secretary of the AMERICAN CHEMICAL SOCIETY, who has recently returned to Washington from Europe. During his visits to Germany he discussed the outlook with chemists and officers of the great German chemical cartel.

Like other industries in all European countries, the German dyestuffs industry is at present hampered by inability to get sufficient coal. The plants are in working order, and the technical staffs and the labor of the various companies are intact, Dr. Parsons reported, and with sufficient coal the German dye industry is ready at once to produce to its capacity.

Growth of the dyestuffs industry in the United States, Italy, England, together with the Swiss industry, and the more or less successful efforts which have been made in Japan, France, and other places, has been carefully noted by the Germans, according to Dr. Parsons. Disturbed conditions throughout the world, together with internal conditions in Germany, will, however, prevent the immediate launching of any competitive attack. There seems little doubt but that the Germans believe keen competition is a prospect of the future and are preparing themselves for it.

The War Trade Board Section of the Department of State has requested the Department of Justice to investigate the offering for sale of German colors by several companies. The companies which have offered the German colors for sale have not been granted import licenses, nor have consumers to whom import permits have been granted applied to the board for permission to dispose of part of their supplies. Immediate investigation has been promised by the Department of Justice, but inasmuch as the matter came to official attention only a few days ago nothing has as yet developed.

RESIGNATIONS

Dr. R. C. Tolman has been chosen to succeed Dr. A. B. Lamb, as head of the Fixed Nitrogen Research Laboratory of the Nitrate Division of the Ordnance office of the Army, located at the American University. Dr. Lamb is retiring from his work in the Army to return to Harvard University, which granted him a leave of absence during the war. The change takes effect September 1. Dr. Tolman has been connected with the laboratory as an assistant to the head.

Resignation of Dr. Rodney H. True, as chief of the Drug Plants Division of the Bureau of Plant Industry of the Department of Agriculture, was announced a few days ago. Dr. True is one of many scientific and technical men who have recently left government work for various reasons. Their departure, in practically every instance, however, has been in answer to a much more lucrative offer from private concerns who are willing to pay better for the valuable services which the Government gets for so little.

The resignation of James T. Newton as commissioner of patents and the appointment of Robert F. Whitehead as his successor has been a recent development. Mr. Newton entered the Patent Office on March 10, 1891, as a fourth assistant examiner, and worked his way up until he became head of the office. He is to take charge of the American business of the English patent firm of Marks & Clerk. Mr. Whitehead, who was promoted from first assistant commissioner, entered the Patent Office early in 1902 as fourth assistant examiner and rose by successive promotions. Melvin H. Coulston, of New York, assistant commissioner, was named first assistant commissioner by the President at the same time. He also entered the Patent Office within two weeks of Mr. Whitehead in 1902.

Failure of Congress to grant relief to Patent Office experts has resulted in a continued loss of patent experts to the government service. Coming as it does at this time in the face of largely increased applications for patents, such a depletion of the force can mean only serious delay to the work. "There can be no hope until Congress passes a measure giving us the relief we need," one of the officials of the office said.

The Nolan bill providing for reorganization of the Office did not get final action at the last session of Congress. After a determined fight, Senator Norris, in charge of the bill in the Senate, finally brought it up for consideration during the last hours of the session. In an effort to get it in the technical position of "in conference" between the House and Senate, he accepted, more or less philosophically, amendments which killed the bill very effectively. As passed by the Senate, it actually would reduce the number of employees granted the patent office, and no salary increases are granted. It will have to be amended in conference to conform to the House bill in this connection.

August 14, 1920

LONDON LETTER

By STEPHEN MIALL, 28, Belsize Grove, Hampstead, N. W. 3, England

THE SOCIETY OF CHEMICAL INDUSTRY

The annual meeting of the Society of Chemical Industry was held this year at Newcastle-on-Tyne and was well attended.

The award of the Society's medal to Monsieur Paul Kestner, the popular president of the Société de Chimie Industrielle in France, marks not only our esteem for M. Kestner personally, but also our desire for greater coöperation with our French neighbors. The latter we all desire, but it is not easy of accomplishment. The French have logical minds and their educated men have a felicity of expression and a vividness of thought which the compromising and comparatively awkward British do not readily appreciate or attain. M. Kestner has done much both for French industrial chemistry and for Franco-British understanding.

During the last year or two the chemical engineers in the Society have formed an organization to insure due consideration by the Society of the problems of chemical engineering. They have held some interesting conferences, and on this occasion they had arranged a valuable series of papers and discussions on "Filtration." Several of the papers dealt with the separation of solid and liquids by centrifugal filtration and detailed descriptions were given of the Sturgeon centrifuge, the Sharples centrifuge, the Gee separator, and the Kelly and Sweetland filters. The papers are appearing in the *Journal of the Society* *of Chemical Industry*, and form a valuable addition to British information on the subject. The published information on filtration in this country has hitherto been rather meager, although several papers by Mr. Hatschek are well known.

DINNER TO LORD MOULTON

A pleasant dinner was held in London in July, when a number of chemists and chemical manufacturers entertained Lord Moulton in recognition of the very important services he rendered to this country and our Allies, while Director General of Explosives Supplies for the Ministry of Munitions. After a distinguished career at Cambridge, Lord Moulton took to the law and soon obtained a big practice. He had a large number of patent cases and took a considerable interest in chemistry, of which he has gradually acquired a wide knowledge. At the outbreak of war he had already exceeded the allotted span of three score years and ten, and was probably looking forward to an opportunity of greater leisure; but a time of crisis stimulates such a man to give the nation of his best. He quickly realized the necessity of dealing with the dyestuff situation and used his influence with the government to have this properly considered. Before long he was invited to take charge of the supply of explosives, and he threw himself into this work with characteristic energy. He speedily gathered together some of our most learned chemists and most enterprising manufacturers, and coördinated their efforts and organized their energies in a surprising manner. It was also his task to show to the English nation how chemistry went into every portion of its life and how the fibers of its rootlets were inextricably mixed with every industrial enterprise.

When the supply of explosives was no longer an urgent business, Lord Moulton found a fresh outlet for his activities as chairman of the British Dyestuffs Corporation in which the government was a large shareholder. He has now returned to the judicial work which, like so many other subjects he has touched, he adorns. We understand from the speeches made at the dinner that he intends to urge the chemists over here to unite and work together, and that he will take an active part in supporting the appeal for funds which is now being launched by them.

It is pleasant to find that a man who has done so much, yet finds himself able and inclined to work for the public good. We are reminded how Pasteur, whose life was largely spent in the study of crystallographic relations, of fermentation problems, and finally of bacteriology, after he had attained a ripe age and a world-wide reputation, set himself the task of solving for the good of mankind one further problem, and how he, though not a medical man, discovered the nature of hydrophobia and its cure! Long may such old men set an example to us young men.

THE INDIGO SITUATION

The manufacture of synthetic indigo played havoc with the indigo planters in India and brought their profits down to a vanishing quantity. We understand that the Indian government persuaded the indigo planters to combine together and have their problems investigated by trained chemists, who now report that by improved methods of cultivation, extraction and marketing, natural indigo of a quality superior to synthetic indigo can be produced at a lower cost. This natural indigo has been selling in Asia for some little while and is now coming onto the English market. It will be interesting to find out if it can hold its own in Europe, but the present high price of coal and all its derivatives will afford a good chance.

August 5, 1920

INDUSTRIAL NOTES

At a conference between gasoline wholesalers and the Kentucky State Tax Commission, it was decided that, after August 1, the State Tax of one cent per gallon on gasoline sold in the state would be collected by the wholesaler. Under the former system of collection by the retailers, it was estimated that not half the tax was reported to the Commission. $450,000 annually is expected to be produced, the money going to the state road fund.

The Bureau of Mines Experiment Station is to be removed from Golden, Col., to Reno, Nevada, where it will continue its work in connection with the Mackay Mining School of the University of Nevada. Particular study is now being devoted to the vast deposits of complex ore in that section, which is said to contain radium, thorium, mesothorium, and other radioactive substances.

The United States Producers Refining Company of Dallas, Shreveport, and New York, has secured thousands of acres of oil-bearing shale in Texas, Louisiana, Oklahoma, New Mexico, Colorado, Utah, Oregon, and California, and plans to begin immediately extensive operations in shale development. One plant in California is in operation and ten additional plants of 5,000 tons capacity, each estimated at $1,250,000, are to be built at different points in the west. Tests have shown that the company's shale runs approximately 50 gallons per ton.

The Bethlehem Foundry and Machine Corporation has purchased the business of Stevens Brothers, New York City, retaining the personnel and staff of Stevens Brothers, and will conduct a business as engineers and contractors to the chemical industry at 149 Broadway, New York, N. Y.

The Abbott Laboratories of Chicago, manufacturers of pharmaceuticals and chemicals, have purchased a tract of land near Chicago, where they are erecting a plant for the manufacture of fine chemicals.

An International Conference of Refrigeration, at which 42 governments, states, dominions, and colonies were represented, was held in Paris, June 21, 1920, and resulted in the creation of an International Institute of Refrigeration in Paris, to be supported by the participating states. The aim of the Institute is to stimulate the development of refrigeration. M. Emile Gouault was elected director of the Institute, and M. André Lebon was elected chairman of the executive committee.

During the month of July 1920, 36 concerns with a capital of $50,000 or more were organized to engage in the manufacture or distribution of chemicals, drugs, dyes, etc. The investment in new drugs and chemical concerns during the first seven months of 1920 is in excess of the total for the entire twelve months of 1919, and is only $15,000,000 less than the total for 1917, which is the high mark since 1914.

The Southern Dyestuffs Corporation has purchased six buildings at Nitro, W. Va., formerly used by the Government in the manufacture of smokeless powder, and will manufacture acid colors, direct colors, azo dyestuffs, etc. The Miller Rubber Co., of Akron, Ohio, has purchased 80 acres of land at Nitro, including several buildings, and is erecting other buildings where production is expected to start about November 1. The International Aluminum Company has purchased five government units, and will manufacture fertilizer and other products.

Deliveries of German dyes to Belgium, in accordance with the treaty of Versailles, amounted to 36,326 kilos during the month of April, bringing the total reparation dyes through April to 340,296 kilos. During the first six months of 1920, approximately 387 tons of dyes were imported from Germany into Great Britain, including 150 tons of reparation dyes.

Meigs, Bassett & Slaughter, Inc., of Philadelphia, have taken over the interest of Dr. S. P. Sadtler in the firm of Samuel P. Sadtler & Son, analytical and research chemists, and have incorporated as Samuel P. Sadtler & Son, Inc. Dr. Sadtler will continue with the firm as expert consultant.

The Canadian Industrial Alcohol Company of Corbyville, Ontario, which formerly manufactured whisky as the Corby Distillery Co., is now devoting its entire attention to the manufacture of industrial alcohol, having a total daily output of 20,000 gallons. Molasses which is brought from Cuba is the main raw material.

The American Sugar Refining Co., which has extensive investments in Cuban properties, has recently given a large filter press contract to an American company. The continental type of perforated or corrugated drainage surfaces, which has not given satisfaction under the demands of high extraction in this country, is now giving place to the American type of filter press.

The German government has appointed an official board, called the "Economic Union for Crude Coal Tar and Coal-Tar Products," to supervise trade in crude coal tar, coal-tar oil, fuel oil, briquet tar, and similar products. It is made up of representatives from crude and intermediate factories, and from trade circles, the workmen being also represented, and has power to fix prices, control imports and exports, and work out schemes of distribution.

At a meeting of the shareholders of Brunner Mond & Co., Ltd., the directors were authorized to distribute £100,000 among universities and technical institutions for the furtherance of scientific education and research. This distribution is looked upon as a business investment, to enable the company to obtain the services of men adequately trained for the development of chemical enterprises.

PERSONAL NOTES

Professor **Frederic S. Lee**, at the end of the academic year, retired, at his own request, from the directorship of the department of physiology of Columbia University, and will occupy, hereafter, a research professorship. Prof. Lee sailed for Europe early in July and expects to spend the coming year abroad.

Dr. W. C. Phalen, formerly geologist in the U. S. Geological Survey and mineral technologist in the Bureau of Mines, has been engaged as geologist by the Solvay Process Co., with headquarters at Syracuse, N. Y.

Mr. Leo E. Brown has left the General Testing Laboratory of Kansas City, Mo., where he was employed as assistant chemist, and has taken a similar position in the Navy Department at Washington, D. C.

Mr. Henry Earl Surface, a member of the A. C. S., was killed June 9 in a railroad wreck near Schenectady N. Y. Mr. Surface graduated in 1906 in chemical engineering from Ohio State University. Soon after his graduation he entered the Forest Products Laboratory where he served as chemical engineer in the new laboratory at Madison, Wis., until about a year ago, when he undertook special work for the Treasury Department in connection with the pulp and paper industries. Mr. Surface is author of a series of bibliographies compiled for the Pulp and Paper Association.

Mr. Reeves W. Hart recently resigned from the Leather Section of the Bureau of Standards, and has accepted a position as research chemist at the Benicia Tannery of Kullman, Salz and Co., Benicia, Cal.

Mr. Edwin C. Eberman, formerly chemist at the Fostoria Works of the National Carbon Co., Inc., has taken a position as chemist at the Cleveland plant of Benjamin Moore & Co., paint and varnish manufacturers.

Mr. Albert L. Burwell has resigned his position in the Leather Section, Technical Laboratory of the du Pont Dyestuffs Sales, to become superintendent of the C. H. Kemper Co., tanners, of Westport, Conn.

Professor **Charles H. LaWall** of the Philadelphia Section of the A. C. S. has received the honorary degree of Doctor of Science, from Susquehanna University, Selinsgrove, Pa.

Mr. Lewis Davis, formerly biological chemist in the research laboratory of Parke, Davis & Company, Detroit, Mich., is now associated with the Beebe Laboratories, Inc., St. Paul, Minn., as associate laboratory director.

Mr. Leon J. Frost has severed his connections as chemist and purchasing agent with the Enamel Products Co., Cleveland, Ohio, to take charge of the new enameling plant of the Phillips and Clark Stove Co., Geneva, N. Y.

Mr. W. Raymond Kappes, formerly chief chemist with Berger & Wirth, Inc., Brooklyn, N. Y., manufacturers of printing and lithographic inks, is employed as chemist and ink expert with the Rochester Folding Box Co., Rochester, N. Y.

Mr. Chas. H. Hunt has resigned as assistant chemist of the Washington Agricultural Experiment Station, Pullman, Wash., to accept the position of associate chemist, Department of Nutrition, Ohio Experiment Station, Wooster, Ohio.

After thirty years as a teacher of chemistry, during the last sixteen of which he has been professor of chemistry in the University of South Dakota, **Dr. Alfred N. Cook** has resigned his professorship and will make his future home in southern California.

Miss Lucy L. Finner, formerly student of chemistry at the University of Wisconsin, is now with the chemical department of E. I. du Pont de Nemours & Co., at Wilmington, Del.

Mr. Paul F. Webster resigned his position in the research laboratories of Larkin Company in order to take charge of the refining for the East Aurora Vegetable Oil Refineries, Inc., Buffalo, N. Y.

Mr. Frank J. Andes recently severed his connections with the Cuban American Sugar Co., at their mill in Central Constancia, where he had charge of the chemical control of the mill, and will take charge of the laboratories of the Holly Sugar Corp., Huntington Beach, Cal.

GOVERNMENT PUBLICATIONS

By Nellie A. Parkinson, Bureau of Chemistry, Washington, D. C.

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

CONGRESSIONAL COMMITTEES

Weights and Measures. Establishment of standard and decimal divisions of weights, measures, and coins of the United States. Hearings on H. R. 12,850, March 26, 1920. 35 pp.

Helium. Exportation of helium gas, hearing on H. R. 12,376, May 21, 1920. 72 pp.

Graphite. Information concerning graphite, with bibliography compiled by the Tariff Commission. 28 pp.

Petroleum. Advance in price of petroleum products, letter transmitting report, in response to resolution directing immediate inquiry into the cause of recent advance in prices of all petroleum products. House Document 801, 57 pp. June 1, 1920.

NATIONAL ADVISORY COMMITTEE FOR AËRONAUTICS

Moisture Resistant Finishes for Airplane Woods. M. E. DUNLAP. Report 85. 8 pp. Paper, 5 cents. 1920.

PUBLIC HEALTH SERVICE

A Study of the Relation of Factors of a Sanitary Character to Pellagra Incidence in Seven Cottonmill Villages of South Carolina in 1916. JOSEPH GOLDBERGER, G. A. WHEELER, EDGAR SYDENSTRICKER, AND R. E. TARBETT. 35, 1701–14.

Shipment of Chemicals for Disinfecting Water Supplies. 35, 1761.

FEDERAL BOARD FOR VOCATIONAL EDUCATION

General Mining. A. C. CALLEN. Bulletin 38. Trades and Industrial Series 8. 170 pp. 1920.

Coal Mine Timbering. R. Z. VIRGIN. Bulletin 40. Trades and Industrial Series 10. 104 pp. Paper, 15 cents. 1920.

Safety Lamps, Including Flame Safety Lamps and Approved Electric Lamps. R. Z. VIRGIN. Bulletin 42. Trade and Industrial Series 12. 4 pp. Paper, 10 cents. 1920.

GEOLOGICAL SURVEY

Feldspar in 1918. L. M. BEACH. Separate from Mineral Resources of the United States, 1918, Part II. 5 pp. Published June 28, 1920. There was a decrease of approximately 30 per cent in the quantity of feldspar marketed in this country in 1918, as compared with 1917. The industry was showing a healthy growth in 1916 and 1917 and during the early part of 1918, but later in the year the exigencies of war caused production to decrease.

Barytes and Barium Products in 1918. G. W. STOSE. Separate from Mineral Resources of the United States, 1918, Part II. 17 pp. Published June 28, 1920. There was a decrease in the domestic crude barytes marketed in the United States in 1918 of 25 per cent in quantity from the output in 1917 and of 30 per cent from that in 1916, but the value of the output in 1918 was somewhat greater than that of 1916, and less than that of 1917. The quantity of ground barytes, lithopone, and barium chemicals sold in the United States in 1918 was slightly greater than that sold in 1917. There has been a continued steady growth of these industries in this country since they came into prominence in 1915.

Cadmium in 1919. C. E. SIEBENTHAL. Separate from Mineral Resources of the United States, 1919, Part I. 8 pp. Published June 18, 1920. This report gives the production of cadmium in the United States since the beginning of the industry in 1906, the imports for 1903 and later years, the range of fluctuation in price in 1919, and the yearly average selling price since 1906.

Mineral Production of the United States in 1917. Introduction by H. D. McCASKEY. Summary by MARTHA B. CLARK. Separate from Mineral Resources of the United States, 1917, Part I, 60 pp. Published June 28, 1920. This chapter forms the introduction and summary to the two parts of the report, Mineral Resources of the United States in 1917 (Part I, Metals, and Part II, Non-metals), the individual chapters of which have been reviewed as they appeared.

Geothermal Data of the United States, Including Many Original Determinations of Underground Temperature. N. H. DARTON. Bulletin 701. 97 pp. Paper, 20 cents. Published June 1920. The purpose of this report is to collect all available published data bearing on the rate of increase of underground temperature with increasing depth in the United States, together with several hundred original observations by the author and his associates.

Ground Water in Pahrump, Mesquite, and Ivanpah Valleys, Nevada and California. G. A. WARING. Prepared in coöperation with the Department of Engineering of the State of California. Water Supply Paper 450-C. Separate from Contributions to the Hydrology of the United States, 1919. 31 pp. Published June 12, 1920. The purpose of the investigation was to make a short examination of the region in order to determine, if possible, the relative amount of ground water available and its adaptability to successful farming.

Mica in 1918. W. T. SCHALLER. Separate from Mineral Resources of the United States, 1918, Part II. 66 pp. Published May 24, 1920.

Coal in 1918. Part A, Production. C. E. LESHER. Separate from Mineral Resources of the United States, 1918, Part II. 119 pp. Published May 28, 1920.

Lime in 1918. G. F. LOUGHLIN AND HERBERT INSLEY. Separate from Mineral Resources of the United States, 1918, Part II. 42 pp. Issued June 7, 1920.

Structure, and Oil and Gas Resources of the Osage Reservation, Oklahoma. M. I. GOLDMAN. Bulletin 686-W. 24 pp. 1920.

Potash Deposits in Spain. H. S. GALE. Bulletin 715-A. Contributions to Economic Geology, 1920, Part I. 17 pp. Published June 5, 1920. Production of potash for commercial use from the Spanish field was not expected during 1919, and even with the most favorable conditions potash will probably not be shipped from these deposits before the middle of 1920. The prospect of production to meet Spanish needs seems promising, but it is still too early to estimate with much confidence the future of the Spanish field as a factor in the world production of potash.

The Potash Deposits of Alsace. H. S. GALE. Bulletin 715-B. Contributions to Economic Geology, 1920, Part I. 39 pp. Published June 5, 1920. The report includes an account of the location and access of the potash deposits of Alsace, their history and ownership, the output from the Alsatian field, shipping facilities, geology of the deposits, the nature and quality of the potash beds, estimated reserves of potash in the Alsatian field, a summary of the records of the individual mines, their technology, origin of the Alsatian potash deposit, and a bibliography.

The Ore Deposits of Utah. B. S. BUTLER, G. F. LOUGHLIN, V. C. HEIKES AND OTHERS. Professional Paper 111. 672 pp. Paper, $1.50 1920.

BUREAU OF MINES

Manganese, Uses, Preparation, Mining Costs, and the Production of Ferro-Alloys. C. M. WELD AND OTHERS. Bulletin 173. 209 pp. Paper, 30 cents. The bulletin is in 11 chapters, each comprising a separate report, as follows: General information regarding manganese; uses of manganese other than in steel making; problems involved in the concentration and utilization of domestic low-grade manganese ores; preparation of manganese ore; leaching of manganese ores with sulfur dioxide; the Jones process for concentrating manganese ores—results of laboratory investigations; cost of producing ferromanganese ores; production of manganese alloys in the blast furnace; national importance of allocating low-ash coke to the manganese-alloy furnaces; electric smelting of domestic manganese ores; and use of manganese alloys in open-hearth steel practice.

Accident Prevention in the Mines of Butte, Montana. DANIEL HARRINGTON. Technical Paper 229. 59 pp. Paper, 10 cents. 1920.

Safe Storage of Coal. H. H. STOEK. Technical Paper 235. Paper, 5 cents. Issued June 1920.

Indicators for Carbon Dioxide and Oxygen in Air and Flue Gas. L. H. MILLIGAN, D. O. CRITES, AND W. S. WILSON. Technical Paper 238. 23 pp. Paper, 10 cents. Instruments designed in the chemical research laboratory at the Pittsburgh Experiment Station of the Bureau of Mines are described. As a result of this investigation, three instruments have been developed—one for carbon dioxide in air, one for carbon dioxide in flue gas, and one for oxygen in air.

Use of Stenches as a Warning in Mines. S. H. KATZ, V. C. ALLISON, AND W. L. EGY. Technical Paper 244. 31 pp. Paper, 10 cents. An apparatus for measuring intensity of odors was devised for the laboratory examination of various stenches. Of 24 chemicals examined, butyl mercaptan, ethyl mercaptan, amyl acetate, butyric acid, and valeric acid were found most promising for mine warnings.

BUREAU OF STANDARDS

Inks: Their Composition, Manufacture, and Methods of Testing. Circular 95. 24 pp. Paper, 5 cents. Issued June 28, 1920. This circular contains a discussion of the composition and manufacture of inks, and the analytical procedures used in their examination. The methods are not original, but are compiled from a variety of sources, and modifications have been introduced when necessary.

COMMERCE REPORTS—JULY 1920

The prohibition against the importation of dyes, not made in the British Empire, into the Straits Settlements has been temporarily suspended. (P. 1)

Interest is evinced in Shanghai in the importation of **compressed gases**, especially oxygen. (P. 25)

There has been a very serious check in the development of the Italian **sulfur** industry. The production has been cut from 330,000 tons in 1914 to 180,000 tons in 1919. (P. 29)

Progress is being made in Hawaii in the development of a substitute **motor-fuel alcohol** obtained from molasses and the waste of pineapple canneries. (P. 45)

It is reported that the greatest potential source of **turpentine** and **resin chemicals** lies in British Columbia. (P. 74)

It is reported that the use of **stainless steel** will become absolutely necessary in many articles and machinery exported from the United States. (P. 77)

The **nonferrous mining** industry of the United Kingdom is reviewed, based on the report of the committee appointed by the government board of trade to investigate the question. (Pp. 106–11)

A shortage of **gasoline** in the German automobile industry is reported. (P. 130)

The British government is conducting wide researches to discover a **liquid fuel** that will combine satisfactory features from both a scientific and practical viewpoint. (Pp. 134–5)

The **mineral resources** of Armenia are reviewed. (P. 138)

The French **iron** and **steel** industry is reviewed, and statistics are given showing the production of these metals by industrial regions. (Pp. 144–9)

The annual production of **indigo** in Manchuria approximates 4,000,000 to 5,000,000 lbs. (P. 151)

The first shipment of **wood oil** in bulk from Hankow to the United States left there in May. (P. 151)

The manufacture of **spelter** is now being carried on in connection with the hydroelectric power scheme installed by the Tasmanian government. It is proposed to extend the manufacture to zinc shavings, zinc dust, zinc chloride, etc. (P. 153)

The Tunisian **salt** industry has been stimulated by the prospect of large foreign sales. (P. 159)

A revival of the **kauri-gum** industry of New Zealand is reported. (P. 167)

The annual estimate of the **raw-silk** production of the world shows for 1919 a decline of 3,430,500 lbs. from the production of the preceding year and of 6,239,100 lbs. from that of 1917. (P. 175)

The 1918 output of the Canadian **fertilizer** industry includes 27,985 tons of complete fertilizers; 10,934 tons of ammoniated fertilizers; and 27,384 tons of basic slag. This is an increase of approximately 10 per cent over the previous year. (P. 179)

The **vegetable-oil-bearing** industry of Manchuria is reviewed. This trade has been favorably affected because of the increased demand by the United States for these products. (Pp. 180–5)

An American firm has just completed the construction of an **olive oil** storage warehouse in Malaga. It contains 24 subterranean tanks, with a total capacity of 1,000,000 kilos of oil. (P. 189)

It is estimated that the exportation of **pulp** and **paper** from Finland in 1920 will be four times that of 1919. (P. 199)

In 10 months ending October 1919, the United States took 124,339 tons of **rubber** from the British Indies, an increase of 30,904 tons over the amount supplied during the corresponding period in 1918. (Pp. 205–6)

Experiments conducted at the Bureau of Science, Manila, indicate that the production of **sugar** from the **nipa palm** sap would be a commercial success. The manufacture of alcohol from the same source is a well-established industry. (Pp. 212–3)

The outlook of the Finnish **tar** industry for 1920 is very discouraging. (P. 231)

Phosphate, which is virtually the soil itself, is the only mineral produced in or exported from the Society Islands. (P. 233)

The installation of an extensive distillation plant for the recovery of **benzene** and other valuable by-products of coal **tar** is being planned in Australia. (P. 237)

The British **Cutlery** Trades Research Association has agreed that the best and most efficient method of reviving the trade is to have (1) a research association to develop and devise new machinery and methods, and (2) an engineering factory where this machinery can be made efficiently and accurately. The first object has been achieved, and important steps have been taken to secure the second. (Pp. 244–5)

An **oil well** which produces 400 gallons of oil an hour has recently been discovered in Formosa. (P. 246)

The discovery of an extensive deposit of **ocher** and **sienna** at no great distance from the surface and within 30 miles of Adelaide, South Australia, has attracted much local interest, particularly in view of the abnormally high price of imported paint pigments. Samples of the ochers have been forwarded to England, and arrangements have been made through a British house to place the material on the English market. (P. 251)

A new **starch** factory has recently been registered in the Transvaal which will have a daily consumption capacity of about 40,000 lbs. of corn, and will produce starch, corn oil, and cattle feed. Later it will take up the manufacture of glucose. (P. 251)

There is a French export embargo on **foundry pig** and **forge pig** containing less than 15 per cent of manganese, and spiegel iron, containing from 15 to 25 per cent of manganese, and waste and scrap iron which can be utilized only for resmelting. (P. 257)

The Japanese Camphor Monopoly Office has made the same allotment of **camphor** to the United States for the period of July, August, and September 1920, in both quantity and price, as for the preceding quarter. (Pp. 257–8)

The following table shows the area and fuel content of Ireland's **peat** deposits:

Description	Area Acres	Average Depth Feet	Anhydrous Peat Tons
Flat bogs in central belt	726,000	18.66	1,640,000,000
Flat bogs outside central belt	287,000	13.32	460,000,000
Flat bogs unsurveyed	635,000	10.00	770,000,000
Mountain bogs	1,380,000	5.00	830,000,000
TOTAL	3,028,000	...	3,700,000,000

(Pp. 294–5)

German farmers are complaining of the serious shortage of **nitrogen fertilizers**. (P. 303)

The War Trade Board Section of the Department of State announces that General Import License PBF 37, as revised and extended, now permits the **importation** into the United States from all countries of the world without individual import licenses of all commodities excepting synthetic organic drugs, synthetic organic chemicals, dyestuffs, products derived directly or indirectly from coal tar, including crude and intermediate products and mixtures and compounds of such products, for the importation of which commodities individual import licenses will continue to be required. Native drugs and chemicals in their earthy state, as mined or grown, may be imported into the United States from any country in the world without a license. (Pp. 306–7)

France should be a good market for American **steel** until French manufacturers are able to secure a cheaper source of coal. (P. 308)

The production of **potash salts** in Alsace in 1919 was 591,471 tons, an increase of about 65 per cent over the 1913 production. (P. 308)

The delivery of German **dyes** to Belgium, in accordance with the stipulations of the treaty of Versailles, during the month of April amounted to 36,326 kilos. (P. 317)

The German **paper** industry is seriously handicapped by the scarcity and increased prices of raw materials, particularly old paper and rags. (Pp. 321–2)

There was a marked reduced output of **minerals** in Queensland during 1919. With the exception of gold, the reduced output does not in any way indicate a decline in the mineral resources of the state. (Pp. 344–5)

Evidence continues to accumulate that the long-sustained upward movement in the value of **metals** has received a check and a definite reaction has taken place. (Pp. 350–1)

The total French production of **iron ore** during 1919 is estimated at 9,429,689 metric tons, of which 91.2 per cent was produced in the Lorraine basins. (P. 358)

British scientific investigations have demonstrated that **artificial wool** is unsuitable for use in the spinning of yarn on the worsted principle, though there may be some scope for the employment of the fiber in the woolen industry. It is impossible to produce from artificial wool a fabric comparable with one composed of pure wool. (P. 359)

Before the war the **tanning** and leather industry was one of the most important in Lithuania, but at the present time many of the tanneries are idle or are so short-handed that they operate in a more or less primitive fashion. There are also many household tanneries. (P. 383)

The Rubber Growers' Association (Inc.) of London is offering certain sums of money for ideas and suggestions for extending the present uses or for encouraging new uses of **rubber**. (P. 397)

The Italian export **embargo on leather** has been removed. (P. 401)

Large deposits of **copper ore** have been discovered in Northern Finland, and geological examinations have shown that the copper near the surface is rich. (P. 414)

At present the total monthly output of **plate glass** in France is less than one-quarter of the normal possible production of approximately 85,000 square meters per month. (P. 420)

The proposed law to establish a **British Ministry of Mines** is designed to secure "the most effective development and utilization of the mineral resources of the United Kingdom and the safety and welfare of those engaged in the mining industry." (P. 424)

The Bureau of Foreign and Domestic Commerce has received a number of photographs illustrating the various phases of the German **potash** industry. (P. 439)

Despite the paucity of industrial raw materials, the manufacture of **paper** in Italy has attained a considerable degree of importance, and through the utilization of the country's wealth in water power it has been possible to create an active paper industry by importing the major part of the materials required. The United States has come to occupy first place as a source of supply. (Pp. 450–2)

Schemes are being developed in India for the production of about 70,000 tons of **bamboo pulp** for use in the manufacture of paper. (P. 453)

Samples of oil taken from the **oil-bearing shales** of Spitzbergen on analysis proved to contain an exceedingly high percentage of petroleum. There is reported to be great scope for industrial development in the islands. (P. 458)

A number of important British industrial concerns have entered into contracts to secure the products of the **low-temperature carbonization** of coal process. It is hoped by this process to conserve the potentially rich constituents, such as motor spirit or gasoline substitute, fuel oil, sulfate of ammonia, and gas. (P. 459)

An official board has been appointed by the German government for regulating the **coal-tar** trade. (P. 469)

Natalie, the motor fuel, has been in use in South Africa for some time past, and has had many favorable reports upon its practicability as a **gasoline substitute**. It is said to be a by-product of the Natal sugar industry and to be a mixture of power alcohol and ether. (P. 480)

The **rock crystal** trade in South Brazil has been resumed. (P. 502)

Advertisements asking everyone to conserve **gasoline** are being run throughout Canada. In the last few years the demand for crude petroleum has increased more than 650 per cent, while production has increased about 150 per cent. (P. 503)

Artificial **silk** manufacturing at Tomaszow, Poland, is shortly to be resumed. (P. 537)

The production and exportation of **copal gum** in the Belgian Congo is reviewed. (P. 539)

A description is given of the **petroleum deposits** in various districts of Mexico. (Pp. 540–3)

One of the most important features of the new Australian tariff is the removal of the excise duty on **industrial denatured** spirits. The immediate result has been the formation of a company in Australia to manufacture the motor spirit known as natalie. (P. 558)

The following table gives the statistics of the Italian **mining** industry during the four years of the war as compared with the production in 1913:

PRODUCTS	1913 Tons	1915 Tons	1916 Tons	1917 Tons	1918 Tons
Iron ore and manganiferous iron	603,116	679,970	946,604	998,632	694,677
Manganese ores	1,662	12,557	18,147	24,582	31,896
Copper ores	89,847	74,470	88,475	86,842	82,302
Lead ores	44,654	41,590	39,460	39,076	37,583
Zinc ores	158,278	80,622	94,043	79,453	67,116
Iron and copper pyrites	317,334	369,320	410,290	500,782	482,060
Mercury (metal)	1,004	985	1,093	1,071	1,038
Sulfur and sulfur mineral, ground	406,406	380,240	287,965	230,074	253,390
Coal and lignite	701,079	953,082	1,305,840	1,722,157	2,171,397
Petroleum	6,572	6,105	7,035	5,668	4,907
Pig iron	426,754	377,510	467,005	471,188	313,576
Iron and steel	933,500	1,009,240	1,269,486	1,331,641	992,523
Copper	2,091	940	860	1,248	1,114
Lead	21,674	21,812	24,362	16,237	18,332
Zinc	...	.....	258	367	1,188
Antimony	76	548	660	535	367
Aluminium	874	904	1,226	1,740	1,715
Marble	509,342	246,883	200,700	134,233	87,483

(Pp. 563–4)

A shortage of **pig iron** is reported in Scotland. (P. 571)

The production of **talc** in South Africa appears to be a development of the war period. The production for the past few years is as follows: 1913, 1 ton; 1915, 44 tons; 1916, 132 tons; 1917, 785 tons; 1918, 670 tons; and 1919, 757 tons. The talc reserves in the Barberton district are enormous and if properly developed should yield a large tonnage for export. (P. 575)

New Zealand is developing a new industry, the extraction of oil from **Kaun-gum peat**. (P. 586)

The Polish **oil** industry and its prospects are reviewed. (Pp. 601–3)

SPECIAL SUPPLEMENTS ISSUED IN JULY

IRELAND—22*e*
SCOTLAND—22*f*
CANADA—26*a*
MEXICO—35*a*
NICARAGUA—37*a*
ARGENTINA—41*b*
VENEZUELA—51*a*
INDIA—53*a*
BRITISH INDIA—53*f*

STATISTICS OF EXPORTS TO THE UNITED STATES

CEYLON—(P. 7)
- Plumbago
- Rubber

CANADA—(P. 157)
- Paper and manufactures
- Chemical pulp
- Mechanical pulp

AUSTRALIA—(P. 573)
- Oils, fats, and waxes
- Paints and varnishes
- Stones and minerals used industrially
- Ores and metals
- Leather and manufactures
- Drugs, chemicals, and fertilizers

AUSTRIA—(P. 232)
- Fusel oil
- Leather goods
- Iron and steel manufactures
- Talc

LONDON—(P. 403)
- Rubber
- Tin
- Drugs and chemicals
- Aluminium
- Leather
- Gums
- Linseed oil
- Dynamite glycerol
- Scrap metal

HONGKONG—(P. 326)
- Antimony
- Camphor
- Chemicals
- Leather and manufactures
- Peanut oil
- Wood oil
- Aniseed oil
- Cassia oil
- Bismuth
- Manganese
- Wolfram
- Paper and manufactures
- Tin

BELGIAN CONGO—(P. 539)
- Copal gum

NEW PUBLICATIONS

Animal Fats and Oils: Their Practical Production, Properties, Falsification and Examination. Louis Edgar Andés. Translated from the German. 3rd English Ed., revised and enlarged, by H. B. Stocks. 315 pp., 76 illustrations. Price, 15s. Scott, Greenwood & Son, London.

Chemistry: Practical Chemistry: Fundamental Facts and Applications to Modern Life. N. Henry Black and James Bryant Conant. 474 pp. Price, $2.00. The Macmillan Company, New York.

Colloids: Kleines Praktikum der Kolloidchemie. Wolfgang Ostwald and Paul Wolski. 159 pp., 14 illustrations. Price, $1.40. Theodor Steinkopff, Dresden and Leipzig.

Colloids: Les Colloides Mêtalliques: Propriâtés et Préparations. Paul Bary. 95 pp. Price, 5 fr. 50. Dunod, Paris.

Dyes: Application of Dyestuffs to Textiles, Paper, Leather and Other Materials. J. Merritt Matthews. 450 pp. 6 × 9. Illustrated. Price, $4.50. John Wiley & Sons, Inc., New York.

Dyes: The Manufacture of Lake Pigments from Artificial Colors. Francis H. Jennison. 2nd Ed. revised. 172 pp. 9 illustrations. Price, 15s. Scott, Greenwood & Son, London.

Everyday Chemistry. Alfred Vivian. 560 pp. Price, $1.64. American Book Company, New York.

Glass: Le Soufflage du Verre dans les Laboratoires Scientifiques et Industriels. Henri Vigreux. 2nd Ed. 268 pp. Price, 10 fr. Dunod, Paris.

Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists. Superseding Bureau of Chemistry Bulletin 107, revised, and 1916 revisions published in *Journal of the Association of Official Agricultural Chemists.* 400 pp. 6 × 9. Price, $5.00. Journal of the Association of Official Agricultural Chemists, Washington, D. C.

Paint: Analysis of Paint Vehicles, Japans and Varnishes. Clifford Dyer Holley. 203 pp. 5¼ × 8. Price, $2.50. John Wiley & Sons, Inc., New York.

Rubber: Its Production, Chemistry, and Synthesis in the Light of Recent Research. A Practical Handbook for the Use of Rubber Cultivators, Chemists, Economists and Others. Drs. Dubosc and Luttringer. Translated by E. W. Lewis. 8vo. 383 pp. Price, 21s. Charles Griffin & Co., Ltd., London.

Steel: The Making, Shaping and Treating of Steel. J. M. Camp and C. B. Francis. 2nd Ed. 614 pp. Price, $5.00. Bureau of Instruction, Carnegie Steel Co., Pittsburgh, Pa.

Tungsten Steels: A Metallographic Study on Tungsten Steels. Axel Hultgren. Translated from the Swedish. 95 pp. 6 × 9. Illustrated. Price, $3.00. John Wiley & Sons, Inc., New York.

Yeasts. Alexandre Guilliermond. Translated and revised by Fred Wilbur Tanner. 424 pp. 6 × 9. Price, $5.00. John Wiley & Sons, Inc., New York.

RECENT JOURNAL ARTICLES

Alcohol: Recovery of Alcohol from Waste Sulfite Liquor. Ralph H. McKee. *Chemical Age*, Vol. 28 (1920), No. 7, pp. 237–239.

Alcohol: Its Relation to Science and Industry. William L. Crounse. *American Journal of Pharmacy*, Vol. 92 (1920), No. 7, pp. 473–487.

Aluminium: Casting Losses in Aluminium—Foundry Practice in the United States. Robert J. Anderson. *The Metal Industry*, Vol. 18 (1920), No. 7, p. 318.

Ammonia Synthesis: Contributo allo Studio della Sintesi Diretta dell' Ammoniaca. L. Cambi. *Giornale di Chimica Industriale ed Applicata*, Vol. 2 (1920), No. 6, pp. 309–311.

Ammonia Synthesis: Synthesis of Ammonia at High Pressures. Some Notes on the Georges Claude Process. *The Chemical Age* (London), Vol. 3 (1920), No. 57, pp. 56–59.

Blast Furnace: Charts for Computing Blast-Furnace Performances. H. L. Fickett. *Engineering and Mining Journal*, Vol. 110 (1920), No. 3, pp. 108–109.

By-Product Coke: Progress in the By-Product Coke Industry. S. R. Bellamy. *Chemical Age*, Vol. 28 (1920), No. 7, pp. 254–258.

Cement: The Setting of Calcium Sulfate Cements. C. L. Haddon. *Journal of the Society of Chemical Industry*, Vol. 39 (1920), No. 12, pp. 165*t*–168*t*.

Chemical Engineer: Training and Functions of the Chemical Engineer. *The Chemical Age* (London), Vol. 3 (1920), No. 56, pp. 32–33.

Coal: A Comparative Method of Determining the Heat of Carbonization of Coal. Geoffrey Weyman. *Journal of the Society of Chemical Industry*, Vol. 39 (1920), No. 12, pp. 168*t*–169*t*.

Coking Industry: L'Évolution de l'Industrie du Coke Métallurgique aux États-Unis. Ch. Berthelot. *Chimie et Industrie*, Vol. 3 (1920), No. 6, pp. 717–728.

Combustion: Use of Preheated Air for Combustion. John van Brunt. *The Blast Furnace and Steel Plant*, Vol. 8 (1920), No. 8, pp. 473–475.

Copper: The Electrolytic Copper Assay—A New Modification. F. G. Hawley. *Engineering and Mining Journal*, Vol. 110 (1920), No. 4, pp. 162–165.

Copra. P. W. Tompkins. *Cotton Oil Press*, Vol. 4 (1920), No. 4, pp. 53–54.

Cyanamide: Cyanamide Process Plant at Muscle Shoals. Chester H. Jones. *Chemical and Metallurgical Engineering*, Vol. 23 (1920), No. 5, pp. 182–187.

Cyanide: Oxygen in Cyanide Solutions. E. M. Hamilton. *Engineering and Mining Journal*, Vol. 110 (1920), No. 3, p. 116.

Diazo Compounds: The Volumetric Estimation of Diazo Compounds by Reduction. Edmund Knecht and Leonard Thompson. *Journal of the Society of Dyers and Colourists*, Vol. 36 (1920), No. 8, pp. 215–219.

Dyes: Dyestuffs Exports Jump 100 Per cent: New Phases of our Foreign Trade. A. T. Marks. *Textile Colorist*, Vol. 42 (1920), No. 500, pp. 527–528.

Dyes: The Manufacture of Nigrosine. L. O. Koons. *Color Trade Journal*, Vol. 7 (1920), No. 2, pp. 57–58.

Enamels: Relative Action of Acids on Enamels—IV. *Journal of the American Ceramic Society*, Vol. 3 (1920), No. 7, pp. 560–567.

Formaldehyde: Degree of Alkalinity Necessary for the Phloroglucin Test for Formaldehyde. P. J. Hanzlik. *Journal of Biological Chemistry*, Vol. 42 (1920), No. 3, pp. 411–413.

Fuels: Burning Bagasse. Clark Y. McGown. *Combustion*, Vol. 3 (1920), No. 2, pp. 22–24.

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Fuels: The Efficient Burning of Oil Fuel: A Summary of Good Practice. Allen F. Brewer. *Industrial Management*, Vol. 60 (1920), No. 1, pp. 17–22.

Fuels: Recherches Physico-Chimiques sur les Carburants Liquides. Georges Baume, Paul Nicolardot, Paul E. Erckmann, and Henri Vigneron. *Chimie et Industrie*, Vol. 3 (1920), No. 6, pp. 761–768.

Gelatin: Acidity of Ash-free and of Commercial Gelatin Solutions. H. E. Patten and T. O. Kellems. *Journal of Biological Chemistry*, Vol. 42 (1920), No. 3, pp. 363–366.

Heat Balance: Balancing Boiler Heat like Books. A. E. Grunert. *Combustion*, Vol. 3 (1920), No. 2, pp. 16–20, 32.

Iron: Reclaiming Iron from Nonferrous Material. Hubert Hermanns. *The Blast Furnace and Steel Plant*, Vol. 8 (1920), No. 8, pp. 442–447.

Lead: Lead-Smelting Practice at Port Pirie, South Australia. Gilbert Rigg. *Mining and Scientific Press*, Vol. 121 (1920), No. 3, pp. 90–96.

Leather: Determination of Glucose in Leather—1920 Committee Report. J. S. Rogers, Chairman. *Journal of the American Leather Chemists Association*, Vol. 15 (1920), No. 7, pp. 411–433.

Metric System: Why We Should Measure in Meters, Grams, and Liters, without Reservations. Herbert T. Wade. *Scientific American*, Vol. 123 (1920), No. 6, p. 125.

Molybdite: Its Occurrence, Detection and Determination in Partly Oxidized Molybdenite Ores. J. P. Bonardi. *Chemical and Metallurgical Engineering*, Vol. 23 (1920), No. 5, pp. 205–206.

Motor Gasoline from Heavier Hydrocarbons. F. W. Padgett. *Chemical Age*, Vol. 28 (1920), No. 7, pp. 229–233.

Nickel: Alkalinity or Acidity of a Nickel Solution. J. C. Kretchmer. *The Metal Industry*, Vol. 18 (1920), No. 7, p. 309.

Nitrocellulose: The Viscosity of Solutions of Nitrocellulose in Ether-Alcohol. William Howieson Gibson and Robert McCall. *Journal of the Society of Chemical Industry*, Vol. 39 (1920), No. 12, pp. 172*t*–176*t*.

Oils: Catalysis Applied to the Oxidation of Oils. R. S. Morrell. *Journal of the Society of Chemical Industry*, Vol. 39 (1920), No. 12, pp. 153*t*–155*t*.

Paint: An Instrument for Measuring the Hiding Power of Paints. R. L. Hallett. *Paint, Oil and Chemical Review*, Vol. 70 (1920), No. 3, pp. 8, 22–24.

Paper: Research Problems of the Pulp and Paper Industry. D. C. Everest. *Paper*, Vol. 26 (1920), No. 22, pp. 11–14, 30.

Para Rubber Seed as a Source of Oil and Feeding Cake. *India-Rubber Journal*, Vol. 60 (1920), No. 4, pp. 23–24.

Phosphor-Copper: New Process for Making Fifteen Per cent Phosphor-Copper. P. E. Demmler. *The Metal Industry*, Vol. 18 (1920), No. 7, pp. 314–315.

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Sagger Mixtures: A High-Temperature Transverse-Strength Test as a Method of Testing Sagger Mixtures. S. C. Linbarger and C. F. Geiger. *Journal of the American Ceramic Society*, Vol. 3 (1920), No. 7, pp. 543–555.

Silica Glass: Le Verre de Silice: Les Bases Théoriques de l'Industrie. Georges Flusin. *Chimie et Industrie*, Vol. 3 (1920), No. 6, pp. 729–749.

Solders: Gas as an Aid in Manufacture of Solders. Gilbert C. Shadwell. *American Gas Engineering Journal*, Vol. 113 (1920), No. 6, pp. 101–104, 111–113.

TNT: Products of Detonation of TNT. Charles E. Munroe and Spencer P. Howell. *Proceedings of the American Philosophical Society*, Vol. 59 (1920), No. 3, pp. 194–223.

MARKET REPORT—AUGUST, 1920

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

		Aug. 1	Aug. 15
Acid, Boric, cryst., bbls.	lb.	.18	.18
Hydrochloric, com'l, 22°	lb.	.03 ½	.03½
Hydriodic	oz.	.19	.19
Nitric, 42°	lb.	.08½	.08½
Phosphoric, 50% tech	lb.	.25	.25
Sulfuric, C. P.	lb.	.07	.07
Chamber, 66°	ton	22.00	22.00
Oleum	ton	25.00	25.00
Alum, ammonia, lump	lb.	.04	.04
Aluminium Sulfate (iron-free)	lb.	.05	.06
Ammonium Carbonate, pwd	lb.	.16	.16
Ammonium Chloride, gran	lb.	.15	.15
Ammonia Water, carboys, 26°	lb.	.12	.10
Arsenic, white	lb.	.15	.15
Barium Chloride	ton	160.00	160.00
Nitrate	lb.	.11	.11
Barytes, white	ton	30.00	30.00
Bleaching Powd., 35%, Works,	100 lbs.	6.00	6.50
Borax, cryst., bbls	lb.	.10	.10
Bromine, tech., bulk	lb.	.85	.85
Calcium Chloride, fused	ton	27.50	27.50
Chalk, precipitated, light	lb.	.05	.05
China Clay, imported	ton	18.00	18.00
Copper Sulfate	100 lbs.	8.25	8.25
Feldspar	ton	8.00	8.00
Fuller's Earth	100 lbs.	1.00	1.00
Iodine, resublimed	lb.	4.35	4.35
Lead Acetate, white crystals	lb.	.16	.16
Nitrate	lb.	.15	.15
Red American	100 lbs.	.12¼	.12¼
White American	100 lbs.	.10½	.10½
Lime Acetate	100 lbs.	3.50	3.50
Lithium Carbonate	lb.	1.50	1.50
Magnesium Carbonate, Tech	lb.	.13	.13
Magnesite	ton	65.00	65.00
Mercury flask	75 lbs.	88.00	85.00
Phosphorus, yellow	lb.	.35	.35
Plaster of Paris	100 lbs.	1.50	1.50
Potassium Bichromate	lb.	.36	.34
Bromide, Cryst	lb.	.75	.75
Carbonate, calc., 80–85%	lb.	.18	.18
Chlorate, cryst	lb.	.16	.16
Cyanide, bulk, 98–99%	lb.	.30	.30
Hydroxide, 88–92%	lb.	.32	.30
Iodide, bulk	lb.	3.35	3.35
Nitrate	lb.	.15	.15
Permanganate, U. S. P.	lb.	.83	.83
Salt Cake	ton	40.00	40.00
Silver Nitrate	oz.	.60	.61
Soapstone, in bags	ton	12.00	12.00
Soda Ash, 58%, bags	100 lbs.	3.25	3.25
Caustic, 76%	100 lbs.	6.00	6.00
Sodium Acetate	lb.	.12	.12
Bicarbonate	100 lbs.	3.00	3.00
Bichromate	lb.	.24	.24
Chlorate	lb.	.12	.10
Cyanide	lb.	.35	.50
Fluoride, technical	lb.	.18	.18
Hyposulfite, bbls	100 lbs.	4.00	4.00
Nitrate, 95%	100 lbs.	3.90	3.90
Silicate, 40°	lb.	.02	.02
Sulfide	lb.	.10¼	.10¼
Bisulfite, powdered	lb.	.06½	.06½
Strontium Nitrate	lb.	.15	.15
Sulfur, flowers	100 lbs.	3.75	4.00
Crude	long ton	25.00	25.00
Talc, American, white	ton	20.00	20.00
Tin Bichloride	lb.	.21½	.21½
Oxide	lb.	.60	.60
Zinc Chloride, U. S. P.	lb.	.50	.50
Oxide, bbls	lb.	.12	.12

ORGANIC CHEMICALS

		Aug. 1	Aug. 15
Acetanilide	lb.	.60	.60
Acid, Acetic, 28 p. c.	100 lbs.	4.00	4.00
Glacial	lb.	.14	.13
Acetylsalicylic	lb.	.88	.88
Benzoic, U. S. P., ex-toluene	lb.	.85	.85
Carbolic, cryst., U. S. P., drs.	lb.	.15	.15
50- to 110-lb. tins	lb.	.23	.23
Acid (*Concluded*)			
Citric, crystals, bbls	lb.	.80	.80
Oxalic, cryst., bbls	lb.	.60	.60
Pyrogallic, resublimed	lb.	2.35	2.35
Salicylic, bulk, U. S. P.	lb.	.50	.50
Tartaric, crystals, U. S. P.	lb.	.74	.73
Trichloroacetic, U. S. P.	lb.	4.40	4.40
Acetone, drums	lb.	.22	.22
Alcohol, denatured, 190 proof	gal.	1.13	1.13
Ethyl, 190 proof	gal.	7.00	7.00
Wood, Pure	gal	4.40	4.40
Amyl Acetate	gal.	4.00	4.00
Camphor, Jap. refined	lb.	1.20	1.30
Carbon Bisulfide	lb.	.08	.08
Tetrachloride	lb.	.14½	.14½
Chloroform, U. S. P.	lb.	.40	.40
Creosote, U. S. P.	lb.	.75	.70
Cresol, U. S. P.	lb.	.18	.18
Dextrin, corn	lb.	.07½	.07½
Imported Potato	lb.	.12	.12
Ether, U. S. P., conc., 100 lbs	lb.	.24	.24
Formaldehyde	lb.	.50	.49
Glycerol, dynamite, drums	lb.	.28	.28
Pyridine	gal.	2.75	2.75
Starch, corn	100 lbs.	5.75	5.75
Potato, Jap.	lb.	.06½	.06½
Rice	lb.	.25	.25
Sago	lb.	.05	.05

OILS, WAXES, ETC.

		Aug. 1	Aug. 15
Beeswax, pure, white	lb.	.60	.60
Black Mineral Oil, 29 gravity	gal.	.22	.22
Castor Oil, No. 3	lb.	.17	.16½
Ceresin, yellow	lb.	.16	.16
Corn Oil, crude	lb.	.10	.09¼
Cottonseed Oil, crude, f. o. b. mill	lb.	.10	.10
Menhaden Oil, crude (southern)	gal.	.65	.60
Neat's-foot Oil, 20°	gal.	2.00	2.00
Paraffin, 128–130 m. p., ref	lb.	.11½	.11½
Paraffin Oil, high viscosity	gal.	.45	.45
Rosin, "F" Grade, 280 lbs.	bbl.	15.95	15.90
Rosin Oil, first run	gal.	.70½	.73½
Shellac, T. N.	lb.	1.25	1.15
Spermaceti, cake	lb.	.30	.30
Sperm Oil, bleached winter, 38°	gal.	1.85	1.85
Stearic Acid, double-pressed	lb.	.25½	.25½
Tallow Oil, acidless	gal.	1.25	1.25
Tar Oil, distilled	gal.	.60	.60
Turpentine, spirits of	gal.	1.68	1.70

METALS

		Aug. 1	Aug. 15
Aluminium, No. 1, ingots	lb.	.32	.32
Antimony, ordinary	100 lbs.	7.50	7.25
Bismuth	lb.	2.72	2.72
Copper, electrolytic	lb.	.18	.18
Lake	lb.	.18½	.18½
Lead, N. Y.	lb.	.09¼	.09¼
Nickel, electrolytic	lb.	.45	.45
Platinum, refined, soft	oz.	80.00	105.00
Quicksilver, flask	75 lbs ea.	88.00	85.00
Silver	oz.	1.00	1.00
Tin	lb.	.50	.48
Tungsten Wolframite	per unit	6.50	6.50
Zinc, N. Y.	100 lbs.	7.90	8.10

FERTILIZER MATERIALS

		Aug. 1	Aug. 15
Ammonium Sulfate	100 lbs.	5.75	5.75
Blood, dried, f. o. b. N. Y.	unit	8.00	8.00
Bone, 3 and 50, ground, raw	ton	48.00	48.00
Calcium Cyanamide, unit of Ammonia		4.00	4.00
Fish Scrap, domestic, dried, f. o. b. works	unit	7.25	7.25
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%	ton	6.85	6.85
Tennessee, 78–80%	ton	11.00	11.00
Potassium Muriate, 80%	unit	2.25	2.40
Pyrites, furnace size, imported	unit	.18	.18
Tankage, high-grade, f. o. b. Chicago	unit	7.75	7.75

COAL-TAR CHEMICALS

Crudes

		Aug. 1	Aug. 15
Benzene, C. P.	gal.	.35	.35
Cresol, U. S. P.	lb.	.18	.18
Naphthalene, flake	lb.	.18	.20
Phenol, drums	lb	.15	.15
Toluene, 90%	gal.	.35	.35
Xylene, 2 deg. dist. range	gal.	.60	.60

Intermediates

		Aug. 1	Aug. 15
Acids:			
Anthranilic	lb.	2.05	2.05
B	lb.	2.25	2. 5
Benzoic	lb.	.85	.85
Broenner's	lb	1.75	1.75
Cleves	lb.	2.00	2.00
Cresylic, 97–99%	gal.	1.20	1.20
Gamma	lb.	6.00	5.75
H	lb.	2.25	2.25
Metanilic	lb.	1.70	1.70
Monosulfonic F	lb.	3.50	3.65
Napthionic crude	lb.	.85	.85
Nevile & Winther's	lb.	1.90	1.90
Phthalic	lb.	.60	.60
Picric	lb.	.25	.25
Sulfanilic	lb.	.37	.37
Tobias	lb.	2.25	2.25
Amino Azo Benzene	lb.	1.15	1.15
Aniline Oil	lb.	.33	.30
For Red	lb.	.65	.65
Aniline Salt	lb.	.40	.42
Anthracene, 80–85%	lb.	.75	.75
Anthraquinone	lb.	4.50	4.50
Benzaldehyde, tech	lb.	.65	.65
U. S. P.	lb.	1.00	1.00
Benzidine Base	lb.	1.25	1.25
Benzidine Sulfate	lb.	1.15	1.10
Diaminophenol	lb.	6.00	6.00
Dianisidine	lb.	9.00	9.00
p-Dichlorobenzene	lb.	.10	.10
Diethylaniline	lb.	1.75	1.65
Dimethylaniline	lb.	1.30	1.30
Dinitrobenzene	lb.	.36	.36
Dinitrotoluene	lb.	.43	.43
Diphenylamine	lb.	.80	.80
G Salt	lb.	.90	.90
Hydroquinol	lb.	2.25	2.25
Metol (Rhodol)	lb.	6.75	6.75
Monochlorobenzol	lb.	.18	.18
Monoethylaniline	lb.	2.15	2.15
a-Naphthylamine	lb.	.55	.55
b-Naphthylamine (Sublimed)	lb.	2.25	2.25
b-Naphthol, dist.	lb.	.88	.88
m-Nitroaniline	lb.	1.05	1.05
p-Nitroaniline	lb.	1.30	1.25
Nitrobenzene, crude	lb.	.14	.14
Rectified (Oil Mirbane)	lb.	.18	.18
p-Nitrophenol	lb.	.80	.80
p-Nitrosodimethylaniline	lb.	2.90	2.90
o-Nitrotoluene	lb.	.25	.25
p-Nitrotoluene	lb.	1.50	1.50
m-Phenylenediamine	lb.	1.15	1.45
p-Phenylenediamine	lb.	2.55	2.55
Phthalic Anhydride	lb.	.50	.50
Primuline Base	lb.	3.00	3.00
R Salt	lb.	.90	.90
Resorcinol, tech	lb.	3.50	3.50
U. S. P.	lb.	5.50	5.25
Schaeffer Salt	lb.	.75	.75
Sodium Naphthionate	lb.	1.10	1.10
Thiocarbanilide	lb.	.60	.60
Tolidine, Base	lb.	1.75	1.75
Toluidine, mixed	lb.	.44	.44
o-Toluidine	lb.	.35	.35
m-Toluylenediamine	lb.	1.40	1.40
p-Toluidine	lb.	2.00	2.00
Xylidene, crude	lb.	.45	.50

COAL-TAR COLORS

Acid Colors

		Aug. 1	Aug. 15
Black	lb.	1.25	1.25
Blue	lb.	3.00	3.00

Acid Colors (*Concluded*)

		Aug. 1	Aug. 15
Fuchsin	lb.	2.50	2.50
Orange III	lb.	1.00	1.00
Red	lb.	1.30	1.30
Violet 10B	lb.	6.50	6.50
Alkali Blue, domestic	lb.	5.50	5.50
Imported	lb.	8.00	8.00
Azo Carmine	lb.	4.00	4.00
Azo Yellow	lb.	2.00	2.00
Erythrosin	lb.	12.00	12.00
Indigotin, conc.	lb.	3.00	3.00
Paste	lb.	1.50	1.50
Naphthol Green	lb.	1.95	1.95
Ponceau	lb.	1.25	1.25
Scarlet 2R	lb.	1.00	1.00

Direct Colors

		Aug. 1	Aug. 15
Black	lb.	1.00	1.00
Blue 2B	lb.	.70	.70
Brown R.	lb.	1.65	1.65
Fast Red	lb.	3.50	3.50
Yellow	lb.	2.00	2.00
Violet, con't	lb.	2.20	2.20
Chrysaphenine, domestic	lb.	2.25	2.25
Imported	lb.	3.80	3.80
Congo Red, 4B Type	lb.	.90	.90
Primuline, domestic	lb.	3.00	3.00

Oil Colors

		Aug. 1	Aug. 15
Black	lb.	.70	.70
Blue	lb.	1.65	1.65
Orange	lb.	1.40	1.40
Red III	lb.	1.65	1.65
Scarlet	lb.	1.75	1.75
Yellow	lb.	1.70	1.70
Nigrosine Oil, soluble	lb.	.90	.90

Sulfur Colors

		Aug. 1	Aug. 15
Black	lb.	.20	.20
Blue, domestic	lb.	.70	.70
Brown	lb.	.35	.35
Green	lb.	1.00	1.00
Yellow	lb.	.90	.90

Chrome Colors

		Aug. 1	Aug. 15
Alizarin Blue, bright	lb.	7.75	7.75
Alizarin Red, 20% Paste	lb.	1.10	1.10
Alizarin Yellow G	lb.	1.00	1.00
Chrome Black, domestic	lb.	1.25	1.25
Imported	lb.	2.20	2.20
Chrome Blue	lb.	2.50	2.50
Chrome Green, domestic	lb.	2.00	2.00
Chrome Red	lb.	2.00	2.00
Gallocyanin	lb.	3.25	3.25

Basic Colors

		Aug. 1	Aug. 15
Auramine, O, domestic	lb.	2.50	2.50
Auramine, OO	lb.	4.15	4.15
Bismarck Brown Y	lb.	.90	.90
Bismarck Brown R	lb.	1.20	1.20
Chrysoidine R	lb.	.75	.75
Chrysoidine Y	lb.	.75	.75
Green Crystals, Brilliant	lb.	6.00	6.00
Indigo, 20 p. c. paste	lb.	.85	.85
Fuchsin Crystals, domestic	lb.	6.50	6.50
Imported	lb.	12.00	12.00
Magenta Acid, domestic	lb.	4.25	4.25
Malachite Green, crystals	lb.	4.50	4.50
Methylene Blue, tech	lb	2.75	2.75
Methyl Violet 3 B	lb	3.00	3.50
Nigrosine, spts. sol.	lb	.85	.85
Water sol., blue	lb.	.70	.70
Jet	lb.	.90	.90
Phosphine G., domestic	lb.	7.00	7.00
Rhodamine B, extra conc'd	lb.	40.00	40.00
Victoria Blue, base, domestic	lb	6.50	6.50
Victoria Green	lb	6.00	6.00
Victoria Red	lb.	7.00	7.00
Victoria Yellow	lb	7.00	7.00

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CONTENTS

THE CHICAGO MEETING:

A Memorable Council Meeting 938
General Meeting 939
The Value of Technical Training in the Reconstruction of Industries. Thomas E. Wilson 941
The Relation of Educational Institutions to the Industries. Henry P. Talbot 943
The Education of the Research Chemist. Robert E. Rose 947
Qualifications of Organic Chemists. M. L. Crossley. 951

SIXTH NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES:

Opening Address. Chas. H. Herty 956
Progress of the American Coal-Tar Chemical Industry during 1919. Grinnell Jones 959
Reorganization of the Chemical Warfare Post of the American Legion 961
Abstracts from the Meetings 962

ORIGINAL PAPERS:

The Determination of Carbon Monoxide in Air Contaminated with Motor Exhaust Gas. M. C. Teague 964
The Use of Catalysts in the Sulfonation of Aromatic Compounds. Joseph A. Ambler and William J. Cotton 968
Phthalic Anhydride. IV—The Vapor Pressure of Phthalic Anhydride. K. P. Monroe 969
The Effect of Certain Accelerators upon the Properties of Vulcanized Rubber—II. G. D. Kratz and A. H. Flower 971
"Porcelain" White Lead. Edwin Euston 974
Utilization of Kid, Rabbit, Horse, and Seal Meats as Food. Arthur D. Holmes and Harry J. Deuel, Jr. 975
A Chemical Method for the Detection in Fruit of a Prior Frozen Condition. William M. Dehn and M. C. Taylor 977
The Determination of Moisture in Beet-Sugar Factory Products. V. L. Aikin 979
The Determination of Nitrates in Soil. A. L. Whiting, T. E. Richmond and W. R. Schoonover .. 982
The Proximate Analysis of Hardwoods: Studies on *Quercus Agrifolia*. W. H. Dore 984
Nitrate Content of Certain Waters Considered Bacteriologically Safe. M. Starr Nichols 987
Relationship of Hydrogen-Ion Concentration of Natural Waters to Carbon Dioxide Content. R. E. Greenfield and G. C. Baker 989
A New Technical Method for the Estimation of the Saccharogenic Power of Diastatic Preparations. Kokichi Oshima 991
The Analysis of Aromatic Nitro Compounds by Means of Titanous Chloride. F. L. English 994
The Analysis of Molybdenum, Cobalt, and Chromium Alloys. J. R. Camp and J. W. Marden 998
A Rapid and Systematic Method for the Analysis of Light Aluminium Casting Alloys. Russell M. Berry 998

LABORATORY AND PLANT:

Soda Lime as an Absorbent for Industrial Purposes. Robert E. Wilson 1000
The Jelly Strength of Gelatins and Glues. S. E. Sheppard, S. S. Sweet and J. W. Scott, Jr. 1007
Gasoline from Natural Gas. IV—Temperature Correction and Blending Charts. R. P. Anderson 1011

ADDRESSES AND CONTRIBUTED ARTICLES:

Bone-Black and Decolorizing Carbons. W. D. Horne 1015
History of the Preparation and Properties of Pure Phthalic Anhydride. H. D. Gibbs 1017
New Fields of Phytochemical Research Opened Up by the Cultivation of Medicinal Plants on an Economic Scale. Edward Kremers 1018
A Comparison of Accuracy in Analysis of Metallurgical Materials during the Past Twenty-five Years. E. D. Campbell and George F. Smith 1020

SCIENTIFIC SOCIETIES:

Sixtieth Meeting American Chemical Society, Chicago, Ill., September 6 to 10, 1920—Program of Papers; The Chemical Societies in New York City 1022

NOTES AND CORRESPONDENCE:

Better Chemical Nomenclature in Trade Usage; Chemical Reading Courses; Explosion of Flashlight Powders; Composition of Water-Glass Solutions; Automatic Methods of Gas Analysis Depending upon Thermal Conductivity; Stolen Platinum; New Chemical Laboratory for Yale University; New Experiment Station of the Bureau of Mines; Gasoline from Natural Gas. III—Heating Value, Specific Gravity, and Specific Heat—Correction; Alkali Fusions. II—The Fusion of Sodium Benzene *m*-Disulfonate with Sodium Hydroxide for the Production of Resorcinol—Correction; The Prevention of Sugar Deterioration by the Use of Superheated Steam in Centrifugals—Correction 1026
WASHINGTON LETTER 1028
PARIS LETTER 1029
INDUSTRIAL NOTES 1030
PERSONAL NOTES 1031
GOVERNMENT PUBLICATIONS 1032
BOOK REIVEWS 1035
NEW PUBLICATIONS 1038
MARKET REPORT 1039

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THE CHICAGO MEETING

A MEMORABLE COUNCIL MEETING

To one who has attended many, many meetings of the Council of the American Chemical Society that held in Chicago on September 6, 1920, stands out preëminently. It proved beyond a doubt that a large gathering can act as a truly deliberate body. Speakers argued directly to the point, a mass of business was transacted, full opportunity was afforded for presentation of every side of the various subjects under discussion. Where action was proposed which seemed to carry the possibility of danger to the Society as a great national organization the Council stood firm and proved itself thoroughly conservative. On the other hand, where progressive action was called for to meet the needs of the times, the Council did not hesitate to take action.

The official minutes of the meeting are published in full in the Proceedings in the October issue of the *Journal of the American Chemical Society*. Only a few of the more important matters are touched upon here.

FUTURE MEETINGS

The dates for the 1921 Spring Meeting, to be held at Rochester, N. Y , were fixed for April 26 to 29, 1921. The Council will meet on the afternoon of April 25. Invitations for the next Annual Meeting were received from the Pittsburgh and the New York Sections. The matter was referred to the President and Secretary with power to act, the understanding being that should a general meeting with other societies be arranged the invitation of the New York Section would be accepted.

By an overwhelming vote the Council rejected the proposal to hold only one general meeting each year. The reasons which determined this large vote were: There is no lack of invitations on the twice-a-year basis; there is an abundance of material offered for the programs; the policy of meeting in different sections of the country is highly stimulative; and the suggested substitution of intersectional meetings for one general meeting was considered to be a possible wedge which might eventually disrupt the Society. It was voted, however, that the entertainment features of future meetings be simplified, that visiting members participate in the expenses incident to the meetings, and that more time be provided on the programs for the reading of scientific papers.

While expressing appreciation of the invitation to become a charter member of the Federated American Engineering Societies, the Council voted unanimously against acceptance of the invitation. It was deemed preferable for the Society to act in a coördinate relation rather than as an actual member of the Federation. In the same spirit and for the same reasons the Council advised local sections to refrain from joining state and local engineering and technical societies. We shall discuss this latter point more at length in a subsequent issue.

By unanimous vote the following resolution was adopted:

> The Council of the American Chemical Society, regretting that Congress did not pass legislation for the protection of the dye industry in the United States, and inasmuch as the failure to enact such proper legislation has resulted in the withholding and preventing of proper and necessary development, wishes to reiterate its position taken at previous meetings.
>
> *Therefore be it Resolved*, That Congress be urged to take action on this important question at the earliest possible date.

At the request of Brigadier General Amos A. Fries, chief of the Chemical Warfare Service, a committee was appointed to coöperate with that Service. The details are given on page 958 of this issue.

DUES INCREASED

Following a delightful dinner in the rooms of the University Club, the Council resumed its sitting and took up the final matter for consideration, namely, the question of the increase of dues from ten to fifteen dollars. The report of the Finance Committee made clear the fact that the Society was facing a deficit of from twenty to thirty thousand dollars this year. The main cause of this unfortunate situation was the constantly increasing cost of paper and printing. Conditions indicated that for the same reasons this deficit would be even greater during the ensuing year. The testimony of many of the councilors connected with large laboratories showed clearly that the younger men, just graduating from college and entering upon an earning career, were to-day receiving salaries which averaged at least ninety per cent more than the same type of young chemist received five years ago. Therefore an increase of dues to $15.00 would not tax the income of the young chemist of to-day as much as did the $10.00 dues of five years ago. It was recognized that the Society was indulging in no unnecessary expenditures at the present time; a curtailment of the splendid activities of the organization would therefore be necessary if the dues were not raised. The Council thereupon, with only three dissenting votes, adopted the amendment increasing the dues to $15.00, effective January 1, 1921. The Council felt, however, that this action would work a hardship upon one class of men whose financial connection with chemistry was still one of outgo instead of income, namely, graduate students; so in the future all students, whether graduate or undergraduate, are to be given the privilege of membership and receipt of one journal for $6.00, or the same privilege and all three journals for $10.00. The question of defining the word "student" was referred to the President with power.

A feeling of relief passed through the entire body of the Council when the question of raising the dues was settled affirmatively. It was a critical moment in the life of the Society, and the situation was unhesitatingly met. With bankruptcy avoided the Society could go on with no uncertain step to that larger field of effort which the constantly growing importance of chemistry in our country makes imperative. Dr. Coates of the Louisiana Section reported that in advance of the Council meeting that Section, after full discussion, had voted unanimously that the dues should be increased. He predicted that the sentiment in other local sections would be found equally favorable.

GENERAL MEETING

The Sixtieth Meeting of the American Chemical Society opened with the calling to order of the thousand or more members and guests assembled in the Gold Room of the Congress Hotel on the morning of September 7, 1920, Dr. W. Lee Lewis, chairman of the Executive Committee of the Chicago Section, presiding. The address of welcome on behalf of the Section was delivered by the honorary chairman, Dr. Julius Stieglitz.

After a welcome on behalf of the city of Chicago had been extended by Mr. Joseph R. Noel of the Association of Commerce, Dr. Lewis turned the chairmanship of the meeting over to President Noyes, who responded fittingly to the words of welcome, and emphasized the responsibility of the Society in this reconstruction period, particularly in forgetfulness of personal interest in thinking of the great public interest which should be our first concern.

The representative of the Society at the meeting of the International Union of Pure and Applied Chemistry at Rome, Secretary Chas. L. Parsons, gave graphic impressions of the gathering and of the Italian chemical industry. The address delivered by Mr. Thomas E. Wilson appears, in part, pages 941 to 943. Dr. A. S. Loevenhart's address will be printed in the November issue of This Journal.

MEETING AND ENTERTAINMENT AT NORTHWESTERN UNIVERSITY

At this stage of the program a delightful transformation in setting took place. Members and guests boarded special elevated trains, and were taken to the beautiful campus of Northwestern University, at Evanston, where the scientific program was completed in the auditorium of the Patten Gymnasium, a building whose novel architecture fits it admirably for the comfortable seating of large audiences, yet in no wise impairs its value as a gymnasium. Here Professor Talbot read a paper on "The Relation of Educational Institutions to the Industries," and Dr. W. A. Patrick discussed "Some Uses of Silica Gels."

The remainder of the day, and evening, were given over to entertainment features, taking the place of the usual smoker. The broad expanse of campus, bordered on the east by the blue of Lake Michigan, shone upon by the sun of a perfect September afternoon, and gaily decorated with flags and college pennants, was a spot of delightful memory to those privileged to be present. A swimming exhibition in the tank, dancing in the auditorium, a baseball game—Chicago *vs.* The World of Chemists, a band concert, and an organ concert furnished recreation for all and led to a spirit of good-fellowship which extended itself throughout the lawn supper, in which more than a thousand guests participated, and through the evening entertainment which included an orchestral concert, mass singing, and a charming presentation of Sullivan's opera "Cox and Box."

Picnic Supper at Evanston

DIVISIONAL MEETINGS

For the divisional programs of Wednesday and Thursday the setting changed again, this time to the buildings of the University of Chicago. Here the recitation halls of the group of science buildings afforded ample facilities for reading and discussion of reports of progress in the various branches of our science. The officers of the various sections reported interesting meetings, with good attendance. The programs are printed, pages 1022 to 1025.

The name of the Pharmaceutical Division was changed, with the approval of the Council, to Division of Chemistry of Medicinal Products. In this division an informal symposium was held on "The National Research Council and the Chemistry of Medicinal Products." The discussion was opened with a paper by Dr. J. M. Francis, read by Dr. F. O. Taylor. Dr. Francis emphasized the need of coördination of the pharmaceutical research now being carried on in various laboratories. He pointed out how the National Research Council could coöperate with the Division in this matter. Dr. Bancroft outlined some of the outstanding problems, touching particularly upon the need of an understanding of the theories of colloid chemistry in approaching work in this field. He emphasized that the actual work must be done by the research workers in each field, that the National Research Council found its special function the outlining and correlation of problems, and putting workers in the same field in closer touch with each other.

The chairman of the committee of the American Chemical Society on an Institute for Drug Research outlined briefly the progress of the committee's work, and the present problems, and stated that in the near future he felt there would be an announcement of real importance to be made. Dr. F. R. Eldred emphasized the necessity of fostering the research spirit among the pharmaceutical interests, particularly in the universities, and deplored the lack of men of adequate training who are particularly interested in this line of research.

Upon motion of Dr. F. O. Taylor it was

Resolved, That a committee of five, which may be enlarged at the discretion of the Executive Committee of the Division if need be, be appointed to take the papers and suggestions presented, and outline some tentative method whereby the Division can coöperate with the National Research Council, and ask for their coöperation in return, formulate a list of problems of varying degrees of difficulty, and with that work done there will undoubtedly be some further work that will be perfectly evident. Passed.

TRAINING OF DYE CHEMISTS

The Dye Division, having disposed of an extremely interesting program covering not only the results of original research on dyes and intermediates, but papers on the problems of training of men for that particular field, adjourned in regular order, but so interesting a discussion developed after adjournment over conflicting views on this subject that a lengthy informal and purely spontaneous symposium was held, which it is hoped to continue on the regular program of the Rochester meeting.

The especially noteworthy feature of the Leather Section's meeting was the increasing interest of the industries in scientific research, and their willingness to coöperate with university workers.

THE NEW SECTION OF CELLULOSE CHEMISTRY

The formation of a Section of Cellulose Chemistry was the marked event of the meeting of the Division of Industrial and Engineering Chemistry. This decision followed the reading of a series of papers on cellulose, in the second Cellulose Symposium to be held by this Division. Of outstanding value was the paper by Professor Harold Hibbert on "The Constitution of Cellulose."

A symposium on Fuels, led by Dr. A. C. Fieldner of the Pittsburgh Station, U. S. Bureau of Mines, brought out a wealth of important material on the development of new fuels and most efficient utilization of the more common varieties.

The minutes of the meeting are printed below:

The Division of Industrial and Engineering Chemistry enjoyed one of its most successful meetings at Chicago, all sessions being largely attended and the discussion of papers more spirited and extensive than has been usual. The following officers were elected for the ensuing year:

Chairman: H. D. Batchelor
Vice Chairman: C. G. Derick
Secretary: H. E. Howe
Executive Committee: J. G. Vail, Chas. H. Herty, W. F. Hillebrand, Edmund O'Neill, Edward Mallinckrodt, Jr., F. M. de Beers

A committee to consider a plan for encouraging research in educational institutions was reorganized with the following personnel:

W. J. Hale, *Chairman*, F. G. Cottrell, Chas. H. Herty, Henry Howard, George D. Rosengarten

A progress report of the Committee on Chemical Lime was received.

A motion was unanimously passed to ask the President and Secretary of the Society to approve the establishment of a Section on Cellulose Chemistry with the suggestion that Professor Harold Hibbert serve as chairman with G. J. Esselen, Jr., as secretary, until an election can be held.

It was the opinion of the Division that the practice of requiring abstracts was not only beneficial, but that in the future more extensive abstracts should be required. The intention of holding one symposium each meeting on some phase of chemical engineering was also discussed and approved.

The Division of Agriculture and Food Chemistry completed its program early in the day. It is hoped that in the future a more even distribution of material between this Division and the Division of Biological Chemistry may be effected.

Sessions of the Division of Physical and Inorganic Chemistry, Organic Chemistry, and Biological Chemistry brought out the results of intensive research in each of those fields. The Fertilizer Division, Division of Water, Sewage and Sanitation, and Sugar Section, completed their programs within the allotted time, and with profitable discussion of the papers.

In the Rubber Division a committee was appointed to consider the advisability of making some provision for the publication of an annual volume of reprints and lengthy abstracts of everything of interest to the rubber chemist made public during the year, and to report at the next meeting of the Division. Following the reading of the papers a symposium was held on the general subject of rubber analysis, in which many defects in present methods were pointed out. The Division was agreed on the impracticability of devising a scheme of analysis applicable to all samples of compounded rubber. In the round-table discussion of recent developments interest centered on the new Peachey process of vulcanization. It was felt that while the process is theoretically sound, there are many difficulties in the way of its commercial application.

ELECTION OF OFFICERS

Divisional officers for the ensuing year were elected as follows:

Physical and Inorganic Chemistry
Chairman: H. N. Holmes
Secretary: S. E. Sheppard

Industrial and Engineering Chemistry
Chairman: H. D Batchelor
Secretary: H. E. Howe

Biological Chemistry
Chairman: A. W. Dox
Secretary: H. B. Lewis

Chemistry of Medicinal Products
Chairman: Charles E. Caspari
Secretary: Edgar B. Carter

Organic Chemistry
Chairman: Roger Adams
Secretary: H. T. Clarke

Dye Chemistry
Chairman: A. B. Davis
Secretary: R. N. Shreve

Fertilizer Chemistry
Chairman: F. B. Carpenter
Secretary: H. C. Moore

Agriculture and Food Chemistry
Chairman: C. E. Coates
Secretary: T. J. Bryan

Rubber Chemistry
Chairman: W. W. Evans
Secretary: A. H. Smith

Water, Sewage and Sanitation
Chairman: W. T. Mason
Secretary: W. W. Skinner

Section of Leather Chemistry
Chairman: J. A. Wilson
Secretary: Geo. D. McLaughlin

Section of Sugar Chemistry
Chairman: C. A. Browne
Secretary: F. J. Bates

Section of Cellulose Chemistry
Chairman: Harold Hibbert
Secretary: G. J. Esselen, Jr.

The local committee on excursions was successful in arranging series of trips, taking place on Wednesday afternoon and Friday, to many of the industrial chemical plants in Chicago's vicinity, and those who were so fortunate as to participate therein feel that the educational value of these excursions makes them an important feature of the Society's meetings.

On Wednesday evening the annual address of the president was delivered by Dr. William A. Noyes, in the Gold Room of the Congress Hotel. The subject was "Chemical Publications." The address will appear in full in the *Journal of the American Chemical Society.*

ENTERTAINMENT

At the dinner on Thursday evening, with Chairman W. Lee Lewis presiding as a skillful toastmaster, the speakers epitomized the thought of the meeting, namely, the part chemistry is to play in this reconstruction period. Dr. Raymond F. Bacon urged the development of a stronger feeling of professional consciousness among chemists, and recommended the giving of more thought to the business side of chemistry. Dr. Chas. H. Herty emphasized the need of protective legislation, if the progression of the past four years is to continue, and made announcement of the plans for effective coöperation between the civilian chemists of the country and the Chemical Warfare Service through a committee of the ablest members of the AMERICAN CHEMICAL SOCIETY.

President Noyes, whose subject was "Team Work," said that with the assistance of every member we shall be carried forward into that new era, rapidly approaching, when American chemists will lead the world in manufacturing and research.

Mr. Harrison E. Howe, National Research Council sponsor of the tables of physical and chemical constants, urged support for this "tool of the trade" needed by every worker in the chemical field.

Mr. William R. Moss, lawyer and representative of the Chicago Chamber of Commerce, urged that chemists keep in closer touch with "the man on the street," and interest themselves in the daily problems of mankind outside of their own special field.

In closing the program, Dr. Otto Eisenschiml expressed in pleasing manner the gratification it had given Chicago chemists to act as hosts to the parent SOCIETY and guests.

Members of the official bodies of the SOCIETY were entertained at special luncheons by the Chicago members. It was evident that the elaborate plans for the entertainment of the members and accompanying ladies had been carefully laid out in advance, and the Chicago Section is to be congratulated upon the successful culmination of its work.

Opportunity was afforded by the meeting for the getting together of various alumni organizations of chemists, and for a well-attended dinner of Alpha Chi Sigma members. A new feature was a dinner to the professional women in attendance at the meeting, tendered by the ladies of the Chicago Section, at which Miss Ethel M. Terry acted as hostess.

PRESS REPORTS

The offices of the A. C. S. News Service were busy early and late in their efforts to get the salient points of the meeting to public attention through the press. In his report the technical director of the A. C. S. News Service says:

> The reports from the clipping agencies indicate that the publicity given to the Chicago meeting was exceptionally large. Whether it will equal in volume or surpass that received from the St. Louis meeting cannot be ascertained until the full returns are analyzed.
>
> As Chicago is one of the world's greatest news distributing centers, the wires of the Associated Press, the United Press and similar organizations sent out many dispatches to the newspapers of the country, as is shown by the sheaves of clippings now being garnered by the A. C. S. News Service. The admirable dispatch summarizing the work of the meeting, written by Mr. Richard D. Jones of the United Press, had an especially wide distribution. The daily papers throughout Illinois, Indiana, and various parts of the Middle West carried unusually full accounts.
>
> The sixtieth meeting was held in the midst of a political campaign and in a city the press of which happened to be giving more than usual attention to local affairs. The Chicago newspapers, however, printed about ten columns concerning the sessions. The most attention was given by the *Journal*, and the other leading Chicago papers are herewith given according to the space allotted by each: *Tribune, American, Daily News, Post, Herald-Examiner.*
>
> Extensive dispatches were printed in the eastern papers and some of them appeared in prominent positions. The subjects which seem the most popular to date, as far as lay journalism is concerned, are flavoring extracts without alcohol, the resolution urging Congress to pass dye legislation, hydrolyzed sawdust as cattle food, all news relating to fuel and news print, and the announcement that America now makes 800 rare chemicals, this last being featured on the front page of the *New York Times.*
>
> More trade and technical publications sent representatives than ever before in the history of the SOCIETY, because of the fact that so many periodicals of this class are either published in Chicago or have branch offices there.
>
> The A. C. S. News Service wishes to acknowledge the very efficient help of the Chicago Section's Publicity Committee, of which Mr. Chester H. Jones is the chairman.

ATTENDANCE

The following figures tell the story of the total registration:

STATE	MEMBERS	GUESTS	TOTAL
Alabama	1	...	1
Arkansas	1	...	1
California	9	...	9
Colorado	4	...	4
Connecticut	5	2	7
Delaware	12	3	15
District of Columbia	21	8	29
Florida	2	...	2
Georgia	7	2	9
Illinois	404	192	596
Indiana	43	13	56
Iowa	19	6	25
Kansas	9	3	12
Kentucky	2	1	3
Louisiana	7	...	7
Massachusetts	22	6	28
Maryland	7	...	7
Maine	1	...	1
Michigan	28	8	36
Minnesota	20	15	35
Mississippi	1	1	2
Missouri	23	3	26
Montana	1	...	1
Nebraska	10	...	10
New Hampshire	1	...	1
New Jersey	32	3	35
New York	58	7	65
North Carolina	6	2	8
North Dakota	3	...	3
Ohio	88	16	104
Pennsylvania	46	8	54
Rhode Island	1	...	1
Tennessee	3	1	4
Texas	7	2	9
Vermont	1	...	1
Virginia	6	...	6
Washington	2	1	3
West Virginia	3	1	4
Wisconsin	53	11	64
Canada	13	3	16
Cuba	1	...	1
China	...	1	1
England	1	...	1
Japan	1	...	1
	986	319	1305

THE VALUE OF TECHNICAL TRAINING IN THE RECONSTRUCTION OF INDUSTRIES

By Thomas E. Wilson

PRESIDENT, WILSON & CO., CHICAGO, ILLINOIS

I understand that I am the first business man who has been invited to address your SOCIETY. For this privilege I thank you in behalf of industry. It may not be out of place for me to express to you men and women, at this time, the appreciation of industry for the wonderful things that you have done during the past few years, and I want here to make publicly that acknowledgment, particularly to the men of your SOCIETY who have served in our industry, and who did so much to make possible its accomplishments during the war and prior to the war. A great deal has been said of the accomplishments of the men and women of your profession in the preparation of the munitions of war, but probably too little has been said about your great work in industry.

My subject can probably be best treated by outlining briefly the history of chemistry in the packing industry. It is an interesting story and it has been my privilege to have lived through it. The whole story has happened within the lifetime, I think, of every person in this room.

When I first entered the packing business there was no such thing as a chemical laboratory in the Union Stockyards. Many of you are acquainted with the man who opened the first laboratory, Mr. H. B. Schmidt, now of Cincinnati. Mr. Schmidt had his trials and tribulations, I can assure you. His department was looked upon as a luxury. He had a difficult job, but he was shrewd enough to introduce into his laboratory work a vacuum pan for the making of extract of beef. He had been criticised month after month about the expenses of his department, although they were not much, because his room was not larger than ten by ten, and he was the only person in it. When he introduced the vacuum pans he was able to put it on a dollar-and-cents basis and to show results.

As I say, that isn't so many years ago, but I think that was the turning point in the packing industry. Up to that time what were known even then as the large packers were merely butchers. They were a great deal like the cross-roads country slaughter house, improved somewhat, but not to such an extent that they would be recognized to-day.

THOMAS E. WILSON

In the early stages of our industry the butcher had to buy his raw material, the live animal, at such a figure that he could sell the beef resulting from the slaughter at a greater figure than he paid for the live animal. To-day the amount realized for the fresh meat of the animal, the dressed beef, is much less than the purchase price of the live animal. In my estimation, chemistry has made that possible. The manipulation and handling of the products and the development of the products from the lower to the higher levels of value have made it possible for the packer of to-day to sell the beef for a lot less—not a little less—but a lot less than he pays for the live animal.

I am not going into the details of the development of chemistry in the packing industry, but I will show you as an example, just what the development has been in my own concern. As I have said, just a few years ago we started with chemistry in the stockyards, with one chemist. To-day our company has very close to one hundred chemists in their organization. We have the analytical chemist; we have the research chemist; we have the chemical engineering chemist; and last, but not least, the business or commercial chemist, because these men have taught us how to handle our products. They have made possible the distribution of our products all over the world. They started in with refrigeration, with the control of our curing processes, with the control of our canning, and with every step in the industry, and made it possible for this business to develop into the largest industry in the world, to develop to that stage where it was possible to do what was done during the war.

I do not want to take up your time in reciting the accomplishments of the packing industry, but in order to give you a little insight into what those accomplishments were, I am going to read from the report of Stephen Chase, of the Food Administration, which I think pretty well describes the situation.

> * * * * As a result in February 1918 extremely urgent demands were made by the allies for pork shipments to meet the immediate, absolute needs not only of our armies, but the armies of our allies and the civilian population of Europe. In fact, the further prosecution of the war was shown to be directly dependent on the immediate meat supplies being shipped from this country.
>
> At that time a program was worked out in detail, calling for 300,000,000 lbs. of pork products per month for the following three months. It was an undertaking that many people considered entirely impossible, but the program was carried out within 25,000,000 lbs., the total shipment for the three months of February, March and April amounting to 900,000,000 lbs.

That was 900,000,000 lbs. of perishable products in the months of February, March, and April 1918. If you think back you will remember that during that time, particularly when this program started in February, our country was tied up with the greatest snowstorms we have ever seen, and our railroads were practically broken down, but the program, as Mr. Chase says, was carried out.

In addition to that, the application of scientific training in the packing industry has made it possible for this industry to operate on the smallest margin of profit of any industry in the world. That is counter to the common belief, because the information that has been given out has been given out through misunderstandings on the part of many people and unfortunately on the part of some of our government bureaus.

* * * * *

We have in our industry, and I think in practically all of the fundamental industries of this country, reached a turning point. In my opinion, we have passed the point of volume. I know it is true of us, and I think it is true of many of the industries in the country, that we have striven for volume, and in doing this we have in many cases sacrificed our natural resources and our raw material. We must now conserve more than we have in the past. The packers have had credit for using everything but the "squeal," which is true, but I am willing to go on record with you here to-day. There are many fields yet undeveloped, and there are great opportunities, I think, for accomplishments in the future just as great as what have been made up to the present time. These were wonderful. They startled the whole civilized world, but I believe and feel in my heart that the future holds open to men and women of your scientific training—I know it is true in our business—a grand opportunity for further development. This development, however, can come only through close coöperation between men of your training and the business heads and the operating heads of these great concerns. This coöperation will aid not only in the development but also in the conservation of our products and of our raw material, and in the avoiding of spoilage and deterioration.

You chemists have a responsibility, I think, in this respect. I think you have failed a little in bringing your profession before the business people of industry. There has been a little hesitancy and there has also been a disposition to be a little too technical in the discussion of your branch of the work with the business men of your different organizations. In behalf of the business men I bespeak a determination on your part to translate your technical knowledge into the language of dollars and cents, and to talk to the business men in their language, not in your own, and to encourage a closer contact, which I think will be helpful both to you and to business. * * * * *

THE RELATION OF EDUCATIONAL INSTITUTIONS TO THE INDUSTRIES

By Henry P. Talbot

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The announced title of this address was necessarily hastily selected, and is obviously too extensive for the time which can be devoted to it. It is my purpose to talk to you, in homely fashion of a few of the problems which at the moment are confronting the institutions in their attempt to supply industrial needs, with respect to both scientific productivity and man power. There will be much rehearsal of known facts, with, let us hope, an occasional approach from some new angle.

The basic situation seems to resemble closely that of producer and consumer in the commercial field. The two fundamental essentials to successful team-work are an intelligent mutual understanding and a real spirit of give-and-take coöperation. Given these, progress toward satisfactory attainment should be sure.

Henry P. Talbot

At the present time there is too little understanding. Many of us who carry the burdens, as well as the privileges, which are attached to the title "Professor," and live in neighborhoods peopled by business men, the consumers of the college product, are startled and puzzled to find how little these neighbors know of our professional responsibilities or opportunities. Business men talk to our classes and fail to render them the service which they greatly desire to give because they lack experience in exposition. Representatives of the industries attempt to lay down specifications as to the product desired from the colleges without a comprehension of the raw material with which the process begins. Alumni forget their own former crudities and ignore improvements made since their graduation. Teachers, on their side, have much to learn of industrial needs, as will be discussed presently.

Reference has been made to *real* coöperation. Experience indicates that the conception of coöperation in the minds of many is hardly distinguishable from the principle that the only comfortable location for a carbuncle is on the other fellow. It is easy to talk of coöperation, but its realization is very likely to mean some sacrifice of settled routine, with, perhaps, an outlay of energy, or even of money, the ultimate wisdom of which it requires some vision to appreciate. This is as true of the one party as of the other in the field under discussion. It is not as clearly realized as it should be, although there are notable instances of broad sympathy and keen prevision.

The community can demand of the scientific faculties of the colleges, as producers, the maintenance and advancement of work in abstract science; a ready service in all that promotes public welfare; the attack of commercial problems which are vital to industrial progress; and the adequate training of young men and women to meet the demands for workers in these various fields. The successful performance of the last-named service would automatically insure the success of the others, assuming the necessary financial support. The crucial question is: Is the present performance reasonably efficient? It is to be suspected that probably a considerable majority of my present auditors who are employers of college men would promptly answer, "No." I base this assertion upon the trend of discussion heard among groups of men, many of whom are themselves college trained, and upon the fact that Societies, Institutes, and Foundations have been, and are still, devoting much of the time of individuals and committees to the study of the general problem of engineering education, of which chemistry and chemical engineering are phases. In these discussions the indictment seems not to lie so much against the scientific training, especially in the fundamental sciences, as against the attitude of our college graduates (including always, and perhaps particularly, technical schools) toward their co-laborers and their employers. Instructional methods do not, however, escape criticism, which is frequently directed against a too academic atmosphere. It is these two types of criticism which I shall consider with you.

ESSENTIALS DEMANDED OF OUR EDUCATIONAL SYSTEMS

In the report on engineering education which Prof. C. R. Mann prepared for the Carnegie Foundation, there are incorporated the results of inquiries among some five thousand engineers as to the traits which they considered most essential for success in engineering professions. Numerical predominance was overwhelmingly in favor of such attributes as "character," "leadership," "power of initiative," and "resourcefulness," whereas "technical knowledge" occupied about the seventeenth place in a list of some twenty items. Let us recall also what has just been stated as to the apparent present demand for a knowledge of human relations. The inference seems to be that our educational systems should aim to provide these prime essentials, and there is a further implication that there is notable failure in this respect. But, while recognizing the prime significance of such attributes as are enumerated, may we not fairly question whether a charge of general failure is fair to the colleges? Is not the question closely related to that of raw materials? Character which has the elements of permanent excellence, initiative, resourcefulness, and leadership, are all essentially native attributes. The colleges cannot initiate them; they should, of course, develop them where they already exist, but in these days of crowded classrooms and lack of personal contact, the college may, perhaps, deem itself fortunate if, in some instances, it does not interfere with the designs of Providence. For those possessing the qualities of leadership, the colleges can do much toward the development of natural gifts through intelligent encouragement of so-called student activities. In such activities there is opportunity for all to acquire a coöperative spirit and to acquire the ability to present one's personal viewpoint to others. It is, however, probable that greater care should be taken to see that the fellow with real, but latent, traits of leadership, as recognized by the maturer judgment of his instructors, is not debarred from opportunity for development by others with more self-assertion than actual ability. This is a problem for our deans of students.

To meet the alleged deficiencies with respect to human relationships, many advocate a substantial increase in the time allotted to academic instruction dealing with labor problems and "human engineering." It is true that such instruction promises to be greatly vitalized, and there is a growing general recognition of the fact that the engineers of the future must be better informed in matters relating to the welfare and morale of those working with or under them, perhaps even to the exclusion of some engineering training. All this may be granted; and the remedy is good as far as it goes. However, it should not be overlooked that the undergraduate attitude toward the doctrines of the lecture room is, in spite of our best efforts, too often one of genial tolerance rather than of interest, and it should be remembered that most subjects, even professional, are so highly volatile that they seem to leave but little residue after a summer's vacation. It is, therefore, problematical how far academic discussions alone will satisfactorily meet the alleged shortcomings.

In this connection, there should be noted another type of procedure which has been adopted to meet the requirements of the industries for leaders. I refer to the various schools of Business Administration and to courses of the nature of the Course in Engineering Administration as established at the Massachusetts Institute of Technology, the object of which is to afford a systematic training of men for executive positions, giving them a sufficient knowledge of the fundamentals of engineering to enable them to make demands intelligently upon their subordinates, and to appreciate operative needs and propositions for development. This form of training is, as yet, new, but of much promise.

COÖPERATIVE COURSES OF STUDY

But it is quite certain that, do whatever we may, we cannot reproduce the atmosphere or general conditions of the works within the walls of the college or technical school. Moreover, the majority of students have passed without interruption from the primary and secondary schools to the college, and it is probably but natural that the college courses should seem to many but a continuation of the tasks imposed in childhood, to be completed in the easiest possible way. The greater the effort required on the part of the student to secure the privileges of a collegiate training, the greater, in general, and naturally, is the appreciation of the opportunity. Would that the same might be said of sacrifices on the part of the parents! The maximum increase in such appreciation has long been noted in the case of those students whom circumstances have obliged to interrupt college work to accept industrial positions. This has led to attempts to capitalize this accretion of interest by the establishment of coöperative courses in which students alternate between the classroom and an operating plant. As is well known, such courses have long been in successful operation at the University of Cincinnati. Other institutions have developed courses on the same general plan, but varying in details, and to some extent in immediate objective. Two such courses, which are in successful operation at the Massachusetts Institute of Technology, may serve as types. The first, in Electrical Engineering, is conducted in coöperation with the Lynn, Mass., works of the General Electric Company. After two years of continuous work at the Institute, the class is divided into two divisions, each of which is alternately thirteen weeks at the Lynn plant and eleven weeks at the Institute. A minimum amount of classroom instruction is carried on at Lynn coincidently with that service period. The total duration of this course is five years, and upon its successful completion, the degrees of Bachelor and Master of Science are awarded.

The second coöperative course is that including a School of Engineering Practice which immediately follows the completion of the four-year course in Chemical Engineering and covers a period of twenty-six weeks. This, in turn, is followed by twenty weeks of graduate work, including research, in the halls of the Institute. This course has been described in the JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY. At the present time the Stations of the School of Chemical Engineering Practice are established in coöperation with the Eastern Manufacturing Company and the Penobscot Chemical Fibre Company at Bangor, Maine, covering the paper and pulp industry; with the Lackawanna Steel Company and the Larkin Company at Buffalo, where the metallurgy of iron and steel, by-product coke ovens, and the manufacture of soaps are studied; and the Merrimac Chemical Company, the Revere Sugar Refinery, and the Boston Rubber Shoe Company near Cambridge, where the students become acquainted with the manufacture of rubber goods. Each Station is provided with instructional facilities and is under the charge of a resident director, a member of the Institute faculty. The degree of Master of Science is awarded upon the successful completion of this course.

Both of these coöperative courses aim to train, and I believe succeed in training, men of a superior type as engineers, for which there is the most earnest demand and urgent need. Only those men are admitted to these courses who have shown in their earlier work that they have the ability to grasp the significance of the unusual opportunities which such courses offer, and ability to attack the work in a serious spirit and with promise of successfully attaining a standard of accomplishment which may properly be given the recognition of the Master's Degree.

It seems certain that courses of the character of those just outlined must represent distinct advancement toward the satisfaction of the demands made by employers. Nothing could do more to dispel the possibly ultra-academic atmosphere of the college classroom than the atmosphere of the works; nothing can be more useful in the development of the embryonic engineer than to find himself confronted with the necessity of applying the quantitative principles acquired in the quiet classroom to the massive, pulsatory organisms of the operating plant, and to learn the limitations of such applications under the guidance of instructors; nothing could better impress upon the student the fundamental and practical importance of what he is too often prone to regard slightingly as "theoretical stuff," or better reveal to him the ramifications of the knowledge which he will need in his career. And, in these courses, we have, too, the best answer yet devised to the question of training men to understand and handle other men.

I have dwelt upon these coöperative courses mainly that I might emphasize one point in particular, namely, that although when these courses were conceived and planned, there were many who were confident in their predictions that they would not succeed because they would interfere with production, and that the foremen and workmen would tend to resent the intrusion of the students, nothing of the kind has actually happened. Indeed, the story is of a quite different sort. There has been a marked spirit of coöperation on the part of all of the higher types of employee and, so far, no difficulties have arisen when students were temporarily in charge of unskilled laborers. That which has won for them this coöperative spirit is, I think, the evidence which they have given of an honest and earnest desire to learn what the other fellow knew and they did not know. The home letters and verbal statements from students who have participated in these coöperative courses furnish abundant evidence that they have, sometimes unconsciously, acquired much insight into human engineering.

SUMMER EMPLOYMENT FOR THE ENGINEERING STUDENT

But, fine as these courses are, they present one real difficulty. They require five years for completion. It is not, of course, the added tuition, but the living expenses which make the extra year a financial burden. Ignoring now the question whether or not all engineering courses (or at least those of Chemical Engineering) should extend over five years, I desire to make a plea for coöperation on the part of the industries to help out some of our fine fellows who cannot spend this extra year in college. While it may be true that more professional opportunities in chemistry than formerly are open to college men during the summers, it still remains a fact that there is, in the aggregate, a very large body of the finest type of fellows who, each summer, are anxious to gain the same sort of insight into industrial conditions which is gained by their more fortunate associates who take such courses as those outlined above as types, but to whom those opportunities remain closed. I have presented this plea before and have been met at once with the statement that the industries are not philanthropic institutions, and that such men were a trouble and expense. I grant the temporary expense, but I question whether there can be real coöperation without a spirit which is akin to philanthropy, and I even venture to believe that it may well prove to be bread cast upon the waters which will not be so very many days in making its reappearance.

It would obviously be both impracticable and purposeless to undertake to provide for all of the men now entering chemical courses. Very many of these students utterly lack the seriousness of purpose or insight to enable them to realize or to avail themselves of such privilege or opportunity. My query is this: Are there not many of you employers who could take on for the summer a student who had completed two, or better three, years of college work and had the endorsement of his instructors as a man of high character and ability? Give him a pick and shovel, if that is the best that can be done. If he is the right kind of a chap, he will come back to college a better prospective engineer for that experience. But I venture to believe that if you place him as helper to some of your men "higher up" to enable them to undertake some of the things which such men have wanted to get at but could not find time for, you will be surprised to discover how much keen, earnest, intelligent, even if inexperienced, effort will yield. I base this assertion largely upon observations made upon what students have accomplished, when put upon commercial problems in our laboratories between their junior and senior years. It would be the finest sort of a way for you to secure competent men on the later completion of their college courses. Some of these fellows are obliged to secure during the summer the means to defray the expenses of the college year. To them, of course, the question of compensation is of great moment, even though they realize the value of the experience. There are many more to whom the opportunity is paramount to the financial return. I earnestly solicit your interest in this matter as a duty to the profession as a whole, and perhaps to yourselves as well. It is the duty of the colleges to face squarely the demand for more human engineering and to be prepared to scrap age-long habits, if need be, to meet the situation, but it seems to many of us that what is so loudly demanded can be effectively attained only by the opening of more opportunities for actual contact with industrial conditions. The chemical industries have been less responsive than others, because, in part at least, of the belief that their processes needed to be guarded from competitors. This phase should also be candidly studied if it stands in the way of coöperation in your individual case, to determine whether, as a reason, it will stand analysis.

There is still another most important phase of this question which is frequently overlooked to which I desire to call attention. Do we ask ourselves candidly, what were you and I like when we left college? Granted that there has been much improvement in the conception of the college course since our day, is it reasonable that young fellows of twenty-one to twenty-four years of age should issue from four years of training with ability to meet the ideals pictured in many discussions? I do not wish to plead excuses for the college. We can by team-work improve the output, but you of the industries cannot expect to avoid becoming graduate teachers of the men who come to you. This general principle is already admitted by a number of the larger concerns who are offering training schools for young men of college age, thereby making one of the most important contributions toward general improvement. Most plants cannot introduce such schools, but you, as individuals, can constitute yourselves as graduate teachers, and recalling your own immaturity at graduation can exhibit a sympathetic rather than too critical an attitude toward the newly fledged graduate, even going so far as to forgive him if, for the time, he seems to believe that he is the bearer of better tidings than the world has yet heard.

RELATION OF THE INDUSTRIES TO COLLEGE INSTRUCTING STAFFS

Let us now turn to a consideration of the relations to the industries which should exist with respect to the efficient use of the intellectual and physical resources of the members of the instructing staffs of our educational institutions, largely composed as they are of highly trained experts.

No argument is required before this audience in support of the importance of research in abstract science. The really important question is how to increase the output, which means, in turn, how to provide those who are naturally endowed for such research with adequate livings and with necessary equipment. Maximum productivity is probably reached through the endowment of research laboratories, with organizations which enable their members to devote time and thought uninterruptedly to investigational work. Next in order of effectiveness is a provision for essentially uninterrupted work upon the part of individuals who have marked aptitude for research in institutions where a separate research organization is not possible.

The more common, because it is apparently the necessary procedure, is the provision of some facilities for research for a considerable proportion of a teaching staff, the individual members of which vary widely in aptitude and enthusiasm, and all of whom are under a considerable burden of teaching responsibility in these days of crowded classes and a diminished supply of teachers. These research opportunities may take the form of the release of a definite portion of time to be devoted to research, or the provision of a paid research assistant, or the direction of research which is done under a fellowship grant. Obviously, the output under these conditions must be less, as measured in published papers or the magnitude of problems attacked, than in the case of isolated and selected workers in organized research laboratories, but the intangible influence upon the teaching staff which is absolutely essential for a live institution is reflected in the human output.

The industries, through corporate action or through individuals, are showing an increasing interest and generosity toward each of the plans for research just outlined, and it is a pleasure to note that the chemical industries are in the forefront of this movement. The endowments for research laboratories and the activities of the National Research Council have been increased; there is expectation that funds will be contributed to permit a limited number of men of distinction in investigational activity on college staffs to devote themselves entirely to research; and fellowships have been founded at various institutions. The Massachusetts Institute of Technology, for example, holds four of these; one from the du Pont de Nemours and Co.; one from the Monsanto Chemical Co., and two (one called a scholarship) from the Grasselli Chemical Company. Other institutions are similarly fortunate. These fellowships are given without restriction as to the character of the work undertaken, save in one instance to indicate a preference as to the division of chemical science. They have the special merit of inspiration for the holder as well as for those under whose guidance he may carry on his research.

The agencies just outlined contribute mainly to the promotion of the vitally important work in abstract science. How are the institutions helping in the solution of problems which are commonly regarded as those of applied science? The works laboratory can ordinarily provide for the control of the daily operation of the industries and for many questions arising in connection with the improvement of old and the designing of new processes, but it is a rare case in which there are not some problems of this sort, the attack of which is precluded by questions of time, space, or specialized equipment. The up-to-date manufacturer is, moreover, often confronted with questions as to the possible significance or utility of some abstract scientific development with respect to his particular industry. He has no trained specialists at his command and he is, in the words of one of my friends, much in the position of the gentleman attached to the bull's tail, in that he does not know whether he can better afford to hang on or let go. It is to problems of the two latter types that the resources of the institutions may well contribute valuable aid.

The Mellon Institute, with its Industrial Fellowships, is a leader in such industrial coöperation. Other institutions have adopted the same spirit. I will cite but one, that with which I am familiar, the Research Laboratory of Applied Chemistry at the Massachusetts Institute of Technology. In that laboratory a portion of the workers are engaged upon investigations of value to the industries at large, and a portion upon problems presented by individual concerns. The spirit of the so-called "Technology Plan" is the same, but, in that case, the industries have generously done their part first, and at present an organization of forces is being effected to meet the obligations of the Institute.

But, beside those associated with research organizations of the type just indicated, there remains a great body of specialists engaged chiefly in teaching in our various institutions, both colleges and technical schools. What should be the relation of these men to the so-called "commercial interests?" The answer is not simple. I do not know that I can give it to the satisfaction of anyone; but let us look at some of the factors involved. Is there not truth in the frequent assertion that our human product, mainly consumed by the industries, is inefficient in part because too many of us live in ignorance of the conditions which our graduates have to meet; that many have never been confronted with the application of the quantitative principles, about which we discourse fluently, to masses of machinery and materials utterly unlike our beakers and centinormal solutions; that we, perchance, know only of industrial terms as we find them on our library shelves? If there is any truth in such criticisms, may it not be worth while for us pedagogues to consider the possibility of spending an occasional summer in an industrial plant, if the industries will coöperate for our mutual benefit? I frankly confess to a regret on my own part that I did not follow this course years ago. I have, however, had sufficient experience to realize this, that all of you teachers can give a surprising additional vitality to your instruction by drawing upon even a limited personal experience, and I may add that, with discretion, you can make this experience, like your stock anecdotes, last for many years.

Again, we may ask, is it not worth something to any institution to have its instructing staff undertake worth-while commercial problems? Right here we meet divergent opinions. Admitting that dignified investigations with commercial bearings are intrinsically as well worth doing as many of those of abstract science, other factors must also be admitted. Abstract investigations can usually await leisurely solution; the business man, as some one has said, wants his results "yesterday," and this may lead to methods of expediency rather than thoroughness, and may result in encroachments upon time which should be devoted to instruction and study, or it may necessitate extra hours of labor which sap vitality. Contact with commercial work may lead to "pot-boiling" and loss of interest in abstract investigation. The results of industrial research can rarely be promptly published. There is a tradition, a relic of the days before the engineer was admitted to the learned professions, that to come into contact with things commercial is to lose professional caste.

There are, however, brighter tints in the picture. There is a tangible benefit which can come from contact with persons and conditions outside the academic circle. Good judgment will minimize or avoid interference with instructional work. A knowledge of the proper time to slight details to secure results usable for a particular purpose, is as important as a blind, academic superconscientiousness. The industries need this form of coöperation. Moreover, I feel sure that many of my brother administrators will agree with me that we cannot brush aside the importance of association with commercial interests as a means of securing living incomes for teachers and of lessening the present disturbing depletion of the college staffs. I feel that the committee recently appointed by the Council of this SOCIETY to call the attention of educational executives to the need of providing more adequately for the chemists engaged in teaching should have included in their communication some reference to greater liberality in their attitude toward industrial coöperation. The privileges which pertain to academic positions have a real value, but, unhappily, they do not pay grocers' bills, nor do they represent the equivalent of the increased emoluments offered by technical positions, even after advances in college salaries have been made on the basis of recently increased resources. It does not seem reasonable to debar college teachers from remunerative commercial research, which has its own broadening influence.

To avoid a misunderstanding of my position, I must add that I do not advocate a general substitution of industrial research for abstract research. The best interests of both the industries and education dictate that preference should, all things considered, be given to abstract research whenever conditions for such work are adequate as to men, salaries, facilities, and funds. I would, however, plead for the privilege of industrial research for the rank and file of teachers, and express my belief that every teacher is better for some of it. Let us abandon the idea that honest scientific work done for pay subjects the doer to loss of caste, while, at the same time, we honor and admire those who elect to devote mind and heart to those abstract problems which are the real agencies of advancement.

THE FINANCIAL SIDE OF THE PROBLEM

Finally, just a few words as to the financial problems of the educational institutions. It seems to be the fashion for colleges to provide a perpetual bargain counter at which goods are sold at less than cost. In the country-wide drives for endowments much emphasis has properly been laid upon the unavoidable necessity for increasing salaries. It would be easy to infer that the salary roll is the major outlay to be met, while, as a matter of fact, at least for technical instruction, this outlay is equaled or considerably exceeded by the overhead expenses. Indeed, as some one has phrased it, the teacher is in the position of a residuary legatee. Coal bills must be met; labor must be paid for at rates determined by industrial conditions and maintained by collective bargaining; supplies of all sorts must be purchased without the saving influence of the bargain counter; old lines of service must be enlarged and new lines inaugurated. What is then left from the general funds is alone available for salaries, research, old-age pensions, and annuities; that is, for those items which affect the personal status of the instructing staff. Tuition fees now probably provide less than half the actual outlay per student and cannot be raised to cover the other half. These are some of the reasons why colleges have such an insatiable thirst for general funds. Great generosity has been shown toward such institutions, but the present conditions are increasingly perplexing and call for careful consideration and the residuary legatees have their part to perform. As a class, we are prone to over-respect traditional practices. There is much room for improvement in instructional methods in such a way as to reduce the cost per student-hour, to economize space and materials, and to increase the effective use of educational plants throughout the year. Even though we recognize that educational processes cannot successfully be conducted strictly along lines which lead to industrial success, we can easily lean backward by ignoring suggestions obtainable from commercial contacts. It is an unquestionable duty, in these days of reconstruction, to attack such questions courageously—even if some of our hobbies have to go to the scrap-heap. The expedients adopted of necessity during the war to economize were oftentimes surprisingly efficient. We must also give ear to the demand that we should acquaint ourselves and our pupils with the elements of human relationships. Unless we do these things, and do them sincerely, we cannot deserve the support for which we ask.

It is to you who are in the business world that the educational institutions must look for assistance and encouragement. As I have tried to indicate, this can take the form of an increase of appreciation of the fact that the colleges cannot reproduce within their confines the atmosphere of the works, and that we need your coöperation in the development of men both before and immediately after their graduation. To say that we need money for research, for salaries, for operating expenses, for equipment and expansion is, of course, to sound a familiar note. Our corps of science teachers has been sadly depleted as the result of the efficiency shown by such men in national service which marked them as men capable of great accomplishments. You have naturally shown your appreciation of them by offers of positions of great opportunity and high emolument. In chemistry, the demand is so great that the situation is peculiarly critical. We may, I think, in fairness and until the supply of young men has more nearly equaled the demand, as it will presently do, ask you to endeavor to make use of the members of college staffs as consultants without withdrawing them wholly from their activities as teachers, without whose help the supply of capable men will speedily run out. It is not, I think, too much to assert that your financial aid and coöperation of all sorts is your insurance for the future of a most vital sort, and I have no hesitation in speaking for my colleagues, both teachers and administrators, when I say that we shall not be lacking in appreciation or in endeavor to deserve your support.

THE EDUCATION OF THE RESEARCH CHEMIST[1]

By Robert E. Rose

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The education of those who are to lead the dye industry to future successes is a matter of vital interest to us. The subject is equally of interest, in its general aspects, to all who teach and to all who are concerned with commercial enterprises founded on the technical application of the results obtained by research. Its interest to the general public, though not so apparent, is no less real because the methods which are to be suggested for obtaining a sufficient supply of competent chemists are in a large measure applicable to the training of the average citizen.

As we know, the dye industry in this country was established with the aid of chemists who were not trained, except in a general way, for the special needs of the industry. They had to rely on their knowledge of chemistry as a whole in meeting the highly specialized problems of their new vocation. Their adaptability to their new duties throws a very interesting light on the educational system of which they are the products.

It is to-day quite clear to us that the research men trained in this country are competent to hold their own with those produced elsewhere; indeed, it is my own opinion that our chemists, on the average, show more individuality, more independence of thought, and greater adaptability and resourcefulness than those produced by any other educational system; their excellence is the real reason for the present success of the dye industry here. However, our satisfaction should not blind us to the fact that there is still room for improvement; the only safe way to hold a lead is to increase it.

Robert E. Rose

The thoroughness of a man's training shows when he is called upon to use his general knowledge to solve unfamiliar, highly special problems; it is then that he cannot rely on oft-repeated experience, but must think. It is then that the strong and weak points in his training show, because in a large measure clear thinking is a result of proper education. It is for this reason that I think it worth while to describe such weaknesses as were apparent, especially in the less mature men who came almost directly from the classroom. I do so only because I believe that attention to these points will show how they originate and allow of formulating definite policies for improvement.

FAILINGS OF THE AVERAGE YOUNG RESEARCH CHEMIST

Considered as a whole, the first task undertaken by the chemist engaged in founding the dye and pharmaceutical industries here was that of a systematic verification or amplification of facts already in some measure common knowledge. It was his duty to determine the very best conditions for the accomplishment of certain definite ends, the general conditions being known. Work of this kind is essentially a matter of logical experimentation; it involves no necessity for generalization except to a minor extent; it requires logical planning as a prime essential. In attacking work of this kind the research men too often failed, not in attaining the end but in reaching results rapidly enough. They conducted series of experiments, they collected data and yet more data, but they did not discriminate sufficiently between essential information and mere information. They failed quite evidently in a real comprehension of the problem in terms of research. It may be said of them that they were experimentalists first and thinkers second; the real research man experiments to confirm his reasoning. Not having a real grasp of the problem, the chemist too often exaggerated secondary issues and spent time on these without advancing closer to the real object of his work.

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[1] Read before the Division of Dye Chemistry.

Another and a very nearly related failing was that of conducting experiments in a way that allowed of more than one variable influencing, at one time, single members of a series of experiments. I do not refer to the very evident and gross fault of introducing more than one variable intentionally—that was too common—but what I have in mind is that subtler fault of allowing variables to creep in for want of sufficient foresight. It was necessary, let us say, to take the product of a certain reaction and try a number of variants in a subsequent step. Under such circumstances the mature research man would have carried out the first reaction on a scale allowing of a subdivision of a homogeneous mass into smaller portions for the subsequent experiments. What the inexperienced man did was to prepare so small a quantity by the first reaction that he had to make several preparations in order to obtain enough material for the subsequent experiments. Of course, he observed the precaution of carrying out his preparation under what he supposed to be identical conditions, but one does not have to go very far with research to realize how difficult it is to get identical products by carrying out the same reaction twice.

These facts lead me to say, and this in the friendliest possible spirit, that the greatest failing of the chemist, as turned out by the training given him, is an insufficient ability to think logically and to use the structure obtained by thought as a basis upon which to build logical experimentation.

The experience which the young chemist brings with him has not taught him a real grasp of the experimental details of research. He is apt to forget that it is not what you are looking for, which will explain the course of a reaction, but it is frequently an apparently non-essential factor which in reality is of importance. He has not learned that every intermediate step in a series of reactions must be studied carefully and mastered thoroughly in every detail before the next step is approached; that to rush through a series of experiments without paying attention to this point will often necessitate the repetition of the experimental work and, what is worse, lead to false conclusions with regard to the last step. The physical characteristics of every portion of the material which he handles in the whole series, the reactions of the mother liquors, their color, the nature of the precipitates, all these are points he has not learned to fix definitely and exactly in mind and notebook as he goes; he is too apt to neglect them in the hope that he will get quicker results by pushing on to the end.

A great share of the blame for this slighting of detail, one of the two chief faults of the young chemist, is to be attributed to inadequate training in observation. He fails to use his eyes, nose, and fingers as he should; he does not record trifling but very essential differences simply because he never becomes aware of them.

Another cause of this fault is to be found in the impression, which is general, regarding the gross nature of industrial work. Does not industrialism strive for results of importance in the least possible time, and is not the proper method that of taking every short cut? This belief is one of the curses of industrial research. It is one likely to be fostered by technical courses. The younger men were not of a sufficiently robust independence in research matters to resist this impression; they had not learned to think for themselves, and they forgot that in treating industrial subjects, just as in confirming or refuting theoretical conceptions, it is thorough work which gives the quickest results.

The effect of industrialism was apparent in another way which, though of minor importance, still occasioned a great deal of delay. The man who in a college laboratory would have been willing to work with grams had an insatiable desire to work with pounds in a technical laboratory. He lost sight of the fact that the test tube experiment was usually quite enough to decide the majority of points and that the contents of a test tube could be handled much more quickly than quantities necessitating the use of large beakers, flasks, or even small-scale plant apparatus. It should be understood that this is not said with any intention of disparaging large-scale experiments; they are essential, but they should come only after the details of the problem have been satisfactorily solved by experiment on a small scale.

FAULTS OF OUR SECONDARY SCHOOLS

Having emphasized the chief failings of the average young chemist as made evident in the building of the dye industry, it becomes necessary, in order to give any value to these criticisms, to use them as a basis for pointing the way to improvement. First of all, the effort should be made to determine the source of these faults; having established the reason for the trouble, it will then be easier to point out where improvement might be effected.

Logic is judgment and judgment is a matter of sense; the facts which are used in forming judgments will be gaged accurately only if properly observed. The underlying requirement, then, of all research in which data are gathered first-hand, is that of accurate observation, the exercise of well-trained senses; upon this must be built a sound interpretation of the facts observed.

Our education, elementary as well as advanced, makes scarcely an effort to train the senses; instead, emphasis is placed on the development of the memory and of reasoning, though both are really capable of useful development only when there are first-hand observations to remember and conditions which call for the exercise of judgment. Efforts to develop the power of reasoning are essential, because facts in themselves lead nowhere, but it is none the less true that accurate observation is the first requirement.

For the chemist it is of the very first importance to be able to discriminate between slight variations of hue or shade, to recognize minute differences in the macroscopic and microscopic structure of precipitates, to recognize trifling changes in bodies, and to recall them; he should have a delicate sense of touch and of smell. Not only should he be able to recognize these differences absolutely, but he should have sufficient accuracy of observation to judge of them relatively, even when both are not before him at once. He should have a very keen memory for sense impressions. To have such keen senses he must have developed them during the period extending from infancy through the first years of childhood. That the chemist fails so often to observe rightly is thus an outcome of the fact that there is nothing like a concerted effort made by the community to develop the senses through the period of childhood and thus to train the faculty of observation. The evolution of the physical organs of sense is left to chance and in the majority of human beings remains in a very slightly developed condition.

Until a conscious effort is made in our primary education to meet this requirement, our advance in science will not be as speedy as it should. This statement cannot be condemned by saying that foreign men of science have had no better preparation than ours. We cannot afford to remain at the mark set for us. We must go beyond it in this essential matter just as we have in a great many other directions, and earn in this field also the right to call ourselves pioneers.

It is not stating the case too strongly to say that our present methods of primary education, taken as a whole, kill curiosity, dull the senses, and place a false emphasis on the value of information obtained from others. "I know because I have seen, or felt, or heard," that is the mental attitude which we need; not the one which is typified by the statement, "I know because teacher said so," or "because it was in the book." Fortunately, there is every evidence that a new system is coming into effect; already in many communities, especially in the larger cities, great advances have been made, and if the right teachers can be obtained our elementary education will soon be much improved.

The fault continues through all the eight years of school, where the emphasis is consistently on second-hand data. In fact, the emphasis becomes stronger as one reaches the high school years, except in laboratory courses. I have had considerable experience with students in the far West, and these men of the Coast, and women, too, are strikingly good students. To my mind that is only in part a consequence of their mental ability. To a still greater extent, it is a consequence of the fact that they are constantly dealing with nature during their childhood and adolescence. They are accustomed to spending long periods in the woods or on the water directly in contact with nature, where their powers of observation are developed as they are not developed in the city dweller.

FAULTS OF THE INSTITUTIONS OF HIGHER LEARNING

Turning to the institutions of higher learning, the criticism to be offered becomes a little more difficult to formulate. Matters are not quite so bad here, and those that are bad are largely the result of the poor previous training which the student and instructor have had. However, there can be no harm in pointing out the chief faults as I see them. Again, in this kind of work, it is my opinion that only too frequently the requirements can be met by doing routine work. There is very little necessity for reasoning and the student who succeeds best is too frequently one who appreciates just what the instructor would like to have memorized. If we take the courses in chemistry, since that is our chief concern, and analyze them, it seems that they are too much bounded and fixed by the textbook. It is true that in general chemistry, there has been reached something very like standardization in the order followed and in the subjects treated. The fact that the consensus of opinion is satisfied with the present condition seems to point to the conclusion that the subject is fairly well treated, though I cannot recognize any ground for complacency. Most of our elementary textbooks start out by giving the student the basic laws of the science. They force him to contemplate the quantitative aspect of phenomena before he has become familiar with them qualitatively. How many would like the game of bridge if they were required to learn the rules before they were at all familiar with the cards, before they ever attempted to play the game? The same applies to learning chemistry, which is something entirely different from teaching it. I feel that we emphasize logical presentation at the expense of acting in harmony with human nature. In consequence the teacher spends much too much time explaining the text. Of course this is made necessary in some measure by the student's preparation; he does not know how to handle a textbook. But granting that, I think the modern logical textbook is much too abstruse for a beginning class; elaboration is not essential to mental training; difficult problems can be presented simply. To force thinking in unfamiliar terms may be good for the best, but it is bad for the majority of students. Force has no proper place in teaching. Good thinking comes only with liking, and in the universities there is not enough emphasis placed upon kindling the interest, arousing the enthusiasm and maintaining the liking of the students for the subject, and at the same time training them in correct observation and logical thinking. However, with all its weakness, the average course in general chemistry is very much better than the beginning courses in organic chemistry. These use textbooks which are much too encyclopedic as a background for a memory training in graphic formulas, too much rote learning made necessary by too much attention to detail. There is not enough emphasis on the harmony of the whole theory of organic chemistry and not enough on the main features as distinct from the detail. The chief reactions of organic chemistry are very few, but they are made to appear many because each is treated as an individual case in connection with the particular substance being described.

The technical courses in our schools are, on the whole, lamentably inefficient. They are an attempt by those who are not in touch with the industry to prepare a student for the actual conditions to be found in the industry. As they are at present given, most of these could quite well be eliminated and replaced by fundamental subjects, such as English or mathematics. As far as I can learn all those who have the welfare of the industry at heart are very fearful of the swing toward technical courses in colleges and universities. It is the natural outcome of the emphasis on the importance of chemical industry of the past few years, also it is the consequence of the belief among those responsible for the policy of institutions of learning, presidents and governing boards, that they would be showing a willingness to meet the nation's needs by getting away from mere basic education and turning to the production of specialists. Let us hope they will learn the real feeling of those who use young chemists, their wish is that the colleges will insist more than ever that their best service is to give basic courses.

This brings me to another criticism of the university course which is much easier to make than to use as a means of correction. A good research man must have a broad training; he must be familiar with subjects other than chemistry, other than the sciences. He must be able to write his own language clearly and state his conclusions with proper emphasis. But the highest attribute of the human mind is constructive imagination; it is this which, in its greatest perfection, leads to the creation of works of art which add to the beauty of the world, and gives us our great men of science, those whose vision makes possible the formulation of new theories, new interpretations of the universe. In a lesser degree it is essential to all good research, and our educational institutions should strive to develop it. The best food for the growing imagination are the products of man's mind; more effort should then be made to interest the student in becoming familiar with the beauties of music, poetry, and the graphic arts; in his chosen field he should be led to see the grandeur of the achievements of the human mind by a study of the history of the growth of the great theories of science. He should be encouraged to learn more of the other sciences than is usually the case, more especially the biological group, and he should be given an interest in the development of human society. This may seem difficult of accomplishment, but much may be done by a concerted effort on the part of those who have the power to adjust matters, if they will view the matter not as proponents of the value of any one science or art but as champions of the best possible developments of the human mind and body.

CORRECTIVE MEASURES TO OVERCOME THESE FAILINGS

The major faults have been pointed out. What corrections can be suggested? The faults go so far back in the educational system that it seems foolhardy for any one group of men to suggest remedies, but profound modifications require longer, more earnest efforts than shallower ones, and the obvious duty of everyone who desires these changes is to do his utmost to initiate the reforms. These changes, as I see them, revolutionary though they may seem, lie in the path of the evolution and the growth of the educational system. If I am right, then all that I am seeking is to do what I can to accelerate the natural process.

It is very evident that in elementary training there is a wide divergence from that ideal which requires that the innate curiosity of childhood should be fostered and guided to attain that share in the personality of the child and adolescent which is a requisite for the subsequent attainment of the spirit of research.

However, it will only be when average parents become good teachers of observation and deduction instead of dogmatic transmitters of superstitions and half truths that the grave condition can be remedied. In the meantime, we must place every effort behind all that will tend to bring the public to a fuller realization of the enormous national importance of infant and childhood training of a different kind from that at present in vogue. We must do all that we can to introduce a greater respect for accuracy of observation and to promote a better interpretation of facts, especially in the training of the mothers of the nation, upon whom falls so large a share of the burden. Also, we must do all that we can to raise the public appreciation of the dignity and importance of the grade school teacher. We should make it clear that the teacher of childhood is actually of far more importance than the specialist who instructs in the university; of more importance because all the youth of the country passes through her hands and because she has more influence on making good citizens and profound thinkers than the university teacher has. Progress in this is a matter of many years, but let the chemist take an honorably active part in hastening the achievement. We see clearly that there is no other single factor that means so much to real world happiness as good schooling at home and by the state during the years of the developing senses. Even now we should use what influence we may to cause the adoption of policies which will give children a chance to develop their senses, their powers of observation and keep alive in them that healthy skepticism, without which there can be no real thought.

As matters stand, it will be in the institutions of higher learning that changes will commence; it is in them that any influence which we may be able to exert will first make itself felt, because the mass to be moved is smaller and the sciences form a much larger part of the whole. What do we need to make our courses in chemistry better? It is obvious that we must have the very highest grade instructors. We are very fortunate in this respect, but we might do better; and another thing that makes this subject urgent at the present time is that the circumstances connected with the war drew many of the men, who would have become our best teachers, into industrial work. One thing is certain, that we should do everything to make the calling of the teacher of science one which can be embraced without sacrifices such as must be made at present. If it is true that there are chemists in the industries whose activities entitle them to $50,000 a year because of their services to their shareholders or employers, then it is equally true that there are teachers of chemistry who are worth quite as much to the community. The great difficulty is that the teaching profession is in the unfortunate position of not being able to sell its products. It gets only what the users of its products, the community at large, feel called upon to pay. Now we all realize how soon an industry would find itself in difficulties if it allowed its income and profits to be determined by the users of its output. And in the teaching profession the matter is still worse because the users are so indirectly in contact with the teacher that they do not recognize the part he has played in making the product he turns out. I wish that some institutions might refuse to put one penny into new buildings or repairs so long as their staff is in need—it would be proper because a good teacher can get along in a barn but a poor one nullifies the value of palatial equipment. It is needless to say more on this subject here because the SOCIETY has already taken a very definite stand and pledged itself to do all that it can to promote the movement which has already set in to make the reward of the teacher more nearly commensurate with his services.

The suggestion which has been made, and in some cases acted on, that the industries should aid by retaining the services of the professors, is to my mind a very dangerous solution of the difficulty. It amounts to a subsidizing of the teachers by the industry. Research must be entirely untrammeled, and this requires that the college professor keep away from research in the interest of any commercial enterprise. There can be no objection, on the other hand, to his being called in as a consultant, that is, to the use of his wide theoretical knowledge in criticising technical research or solving difficulties, but his functions should go no further than those of a consultant. Only under very special circumstances should the teacher do any research at the direct instigation of an industrial enterprise. It is characteristic of technical research that it is spread over a wide number of subjects and the tendency which will develop if the academician is asked to aid will be simply to scatter his endeavor over so wide a field that the advance of basic knowledge will be retarded. On the other hand, I think it would be extremely advantageous if university men spent some time in direct contact with a technical enterprise in order to keep in touch with the most recent developments in the application of theory to industry. Also this would allow him to learn what demands the industry is placing on his students and would thus enable him to satisfy both sides better without sacrificing his academic freedom in any way. I venture to say that a good number of those who advocate technical courses would change their minds; after such experience they would be convinced that though specialists are essential they cannot be made during undergraduate existence.

SUGGESTED IMPROVEMENTS IN CHEMISTRY COURSES

With regard to improvements in the chemistry courses, I think the first one should be in the matter of textbooks. These should be made with less detail and more regard to the harmony of the whole structure. For example, in the case of organic chemistry, the text is expected to represent what a student should learn in the course of about a year's study, consisting of two lectures, six hours' laboratory work, and perhaps some quizzes weekly. Now, in that time, it is obvious that nothing but the high points can be touched, and the text should be constructed with this clearly in mind. Naturally, this must not be carried too far, but the treatment of a subject should be very different when it is intended only to give a general understanding from that which is required if minute knowledge is to be acquired.

Let us do all we can, then, to aid the genius who will write an elementary organic chemistry that gives little attention to matters of small moment and leaves the student with a feeling for the real meaning of this grand chapter of human knowledge, a book which will leave the student with a live understanding of the evolution of the science, of the meaning of its laws, and a real insight into the facts its symbols represent.

Given a good book, then the lecturer should make it his duty to emphasize the descriptive side of the science. It would be for him to hold the interest of his class, to make them see how tremendously important the subject is in the lives of everyone. Let the textbook explain how the constitution of formaldehyde has been determined, but let the lecturer tell of its manifold industrial uses. If he has any aptitude, he cannot help holding his class and making them anxious to learn even more about the properties of this extremely interesting substance.

In the laboratory, the work should approximate the conditions of research as nearly as possible. Given a good foundation in general chemistry, it should be possible to make each preparation a little research problem. This implies, of course, very small laboratory classes and excellent instructors with a real feeling for research.

Turning to special preparation for industrial work, it seems to me that this is best accomplished by emphasizing the applications of the theories as the theories are unfolded in the ordinary course of presentation. I do not think much emphasis should be placed on a distinction between technical chemistry and theoretical chemistry. After all, it is the latter which is essential for an understanding of the subject. The former can be acquired by experience in actual practice. It is on this account that I think most of the technical courses, as given, fail in their object, and should be improved or eliminated altogether. On the other hand, more especially in the case of the chemical engineer, I feel that a certain familiarity with the names and with the appliances in common use in the industry would be a distinct advantage, and for this purpose I would have special courses in technology given by men who would make it their business to keep in close touch with modern practice.

Surely, it would be possible to take the few chief reactions which underlie the organic chemical industry and talk of these in such a way that both theory and practice would become evident. That is really the kind of technical course which I would endorse.

The chemical industries have been asked to aid by opening their laboratories and plants to the student. The problem is no easy one. It should be remembered that the expense, direct and indirect, of having a student in the industry is very considerable; the return is not so evident. The subject must be discussed further before any general policy can be followed; the industries will certainly meet the teaching profession halfway.

With regard to the rest of the curriculum, what should be done is to introduce as far as possible those subjects which will round out a man, rather than make him a specialist while yet he is an undergraduate. Water analysis may be important, but if it is to be given at the sacrifice of a good course in English, let the English take the place of the water analysis. The same treatment would apply in the case of a number of those courses which are essential applications of chemical technique, rather than intended to widen the student's horizon. This brief comment is all that is allowable here.

The teaching of research is a very high art, and this subject deserves more encouragement in our universities. The fact is that our emphasis is on the teacher rather than the research man, as it most certainly ought to be, but, at the same time, this does interfere with the development of research schools. And research schools are of the very first importance to the development of the science—they are places where the student, working with a number of others, becomes filled with the spirit of research. It was the atmosphere of such schools that made possible the ascendency of Germany in chemical matters. There are men who are much more valuable to the country as leaders of research than as teachers of any subject, and these men should be freed, in so far as possible, from any routine teaching. They will, from very love of their subject, do a great deal of work which is essentially educational. They must, in fact, in order to be leaders of research, but they should not be tied down by any rigid requirements of hours laid down by the directors of the institution in which they are. Furthermore, I should like to see help given to those men who show real ability as investigators while yet they are young, this help to be given before they lose heart and consent to relinquish their dreams of developing really important new lines of research. Let us try to remove the cause of the disheartening feeling that it is not research quality but quantity which is made the criterion of a man's ability. If two men apply for a position, the one that can say he has published ten papers is likely to get it, if the other man can lay claim to only three. Yet those three papers may show a capacity for thought and originality entirely foreign to the numerous articles of his competitor. I have thought that much might be done by the SOCIETY if they would organize some body which would have for its purpose the endorsing of particularly good research, and one which would bring meritorious investigations to the attention of the executives of the institution in which they were done. It seems to me that this would work a great betterment in conditions. To be endorsed by the SOCIETY would mean that a man was recognized, and that students would feel if they went to him that they would be in proper hands. At present, the student looking for a research problem usually drifts to the head of the department, a state of affairs which is not one to encourage the younger men unless they are glad to admit that the head of the department is really the best research man there.

When all is said and done, I feel that we might well adopt the plan which has been so successful in Germany of having institutions set aside for research alone. These should be supported by states and the industries, but should be under no obligation to do research for any special purpose. Their only restriction should be research within the widest interpretation of the science assigned to them.

After the research work is done at the university, the man enters the industry and becomes of immediate interest to us. Can we not improve our methods for handling these men? I feel that the industries are not yet willing to put the emphasis in their research laboratories on research ability as against executive capacity. Both have their place, but actually the former is more important than the latter. What is done is rather to show appreciation of a man's research ability by pushing him into an executive position which, because of its routine duties, prevents his further growth and is a direct loss to everyone.

Another suggestion that I would make is that in those cases where there are a number of technical research men in a laboratory an effort be made to consider this as a school, and a mature man chosen to instruct the less mature men, so that they may have something better than their own mistakes to lead them to improvement. This is an extremely important subject, but in itself would take more time than is available for discussion.

All that I have said of research education is far from conveying my feeling of the intense importance of the subject. I think the SOCIETY has an excellent opportunity of aiding in this matter of national interest. I should like to see, as a beginning, a section devoted to educational subjects where teachers and those who use the products turned out by the teachers could meet to discuss their different views and to formulate plans for betterment.

In concluding I should like to have it understood that I am fully cognizant of the difficulties of teaching, of the trials and disappointments of the profession. I do not wish to seem unreasonable when I say that there is room for improvement before our research men can be all that they should be. Only by having the finest workers in the field of science can we feel entirely secure of our future among the nations. No effort is too great, nothing too small, if it helps to realize the hope that chemistry may come into its own as the most important of the sciences, as a part of that sum of human knowledge which will do more than all else to make life worth living.

QUALIFICATIONS OF ORGANIC CHEMISTS[1]

By M. L. Crossley

Calco Chemical Company, Bound Brook, N. J.

The training of chemists for the organic chemical industry has received considerable attention of late, but it seems to me that their qualifications have not been sufficiently emphasized. A university training is not and should not be considered a sufficient guaranty of the proficiency in chemistry necessary to an understanding and appreciation of the complex problems involved in the manufacture of organic chemicals. It is not the function of an educational institution to produce expert professional men, but rather to train men to think and to orientate themselves advantageously in their environment. To qualify as an industrial chemist, a man's training must be augmented by experience gained in the chemical industry.

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[1] Read before the Division of Dye Chemistry.

During the past few years it has been found necessary to employ men of limited chemical ability and experience, giving them responsibilities which some were unable to appreciate. From the experiences of the past few years we emerge with certain definite convictions concerning the qualifications of chemists for the organic industry.

DESIRABILITY OF A LIBERAL EDUCATION

The man who best understands the past is the man best prepared to evaluate the present and anticipate the needs of the future. Human progress has been slow and difficult. It is unraveled only by a diligent study of the several mediums of human expression. We must convince the public, for in the final analysis the public determines the curicula of our schools, colleges, and universities, that three essential reforms are needed to-day in our system of education—(*a*) less specialization in secondary schools and in the first two years of college work; (*b*) more thoroughness in the teaching of the fundamental studies; and (*c*) a better correlation of studies.

M. L. Crossley

Specialization at too early a period in one's training narrows his intellectual horizon and limits his perspective of world problems. By the time the boys get to college to-day, they are chronic mental dyspeptics. They have had much intellectual hash thrown at them, some of which they have picked up, but very little of which they have retained. The fundamental structure of knowledge, to which they would dovetail the superstructure, is missing. The results are not gratifying. In the future we must insist on a more thorough training in the fundamental studies, particularly in the secondary schools. The efficiency of our educational system can be enhanced by a better correlation of studies and demonstration of their unity of purpose.

The consumer of education's product is responsible for its quality. A liberal education is the best foundation, in my judgment, for scientific work. It cultivates and disciplines the imagination, and is essential in developing a critical and impartial judgment. I believe it was K. Pearson who said that "A disciplined imagination has been at the bottom of all great scientific discoveries." Observation makes possible an outline of the picture and imagination fills in the details, thus completing it, but the composite product of observation and imagination might be a mirage and must be checked by an impartial judgment.

KNOWLEDGE OF FUNDAMENTALS OF CHEMISTRY ESSENTIAL

A knowledge of the fundamentals of chemistry is absolutely essential. The chemical industry will train their chemists to do specific work, but it is imperative that the universities supply them with men who have a sound and thorough knowledge of the fundamentals of chemistry and its allied sciences. It is not sufficient that young graduates have a knowledge of chemical facts. They must also be trained in the methods of research and have an appreciation of its value. We should suggest to our colleges and university faculties that the time now given to industrial courses in chemistry can be more advantageously spent in a thorough study of fundamental organic reactions, quantitative analysis, physicochemical principles, and in a study of the relation of chemistry to world progress. The outstanding weakness of the young college graduate is not his lack of knowledge of industrial processes, but rather his inability to apply fundamental principles to a solution of the problems in hand, particularly when this involves any analytical concept. Industrial research must be thorough. All products of a reaction must be identified and quantitatively determined. The main question is not, "Has a reaction taken place," but "Is it a profitable method of making the product, and what is the mechanism of the reaction?" Can a better method be developed which is simpler and cheaper?

An organic chemist must have his powers of observation highly developed. This should be an essential part of his training. There has been too little attention paid to original and accurate observation on the part of the student. It is only by experimentation under proper guidance that a student gains self-reliance and thus strengthens his powers of initiative. By a too close study of a textbook he learns to rely on authority and neglects his own powers of observation and ability. Initiative is indispensable in an industrial chemist, who is responsible for the creation of processes which must be profitable. Initiative is that dynamic force which is necessary to compel a man to venture beyond the border line of certainty into the unknown and dare to show his individuality. Creative work is impossible without it. Of course the university cannot be expected to create either the powers of observation or initiative in students. These qualities can only be developed. The student must possess them as inheritances. I believe it was Paracelsus who first said that "The power to recognize and value truth cannot be conferred by academic degrees."

The savage was undoubtedly a keen observer, but his interpretations of his observations were not always good for those less savage than he. The university teacher must impart to his students dexterity in experimentation, accuracy, and precision in recording observations, and must cultivate in them an appreciation of the importance of facts. To see and to think are equally important. Facts are the building stones of chemistry. The university must train chemists in the method of grouping and associating facts for retention. Important facts must be memorized and the student must be trained to distinguish quickly relevant from irrelevant facts. Incoherent thinking is usually the result of careless observation and faulty grouping of facts. A chemist must be capable of reading foreign languages—at least German and French—and must have a thorough appreciation of the value of chemical literature. He must be trained to abstract scientific information from the technical journals; to arrange his information systematically in an orderly report; to make a critical study of it; to interpret its meaning, and to apply the results either in shaping the course of research or in interpreting experimental results. No intelligent research can be conducted on any problem until the investigator is familiar with all the work previously done by other investigators on the same or allied subjects.

CHARACTER AN INDISPENSABLE QUALIFICATION

Character is one of the most essential qualifications of a chemist. However much chemistry a man knows, if he is dishonest, particularly in his thinking, selfish, jealous, untruthful, immoral, lacking in ambition and in other essential attributes of character, he will find no place in the chemical industry. If he has character, he may overcome other limitations. He must also be ambitious, for without ambition he is like a candle without a wick. Both fall down under fire. Loyalty to ideals is also essential. Without loyalty a man gives up at the first sign of discouragement. In research, one must have ability to recover from the shock of discouragement and will to try again with undaunted spirit. Of course the young chemist does not ever consider the possibility of failure, and when failure comes he is taken by surprise. The valuable man in an organization is he who recognizes that it is not necessarily a mistake which leads to failure, but rather inability to profit by the mistake. An error in judgment places one man on guard against a similar occurrence, while it unnerves another. It is essentially the function of the institutions of learning to eliminate the undesirable in the process of education. An academic degree should be an endorsement of a man's character as well as an affidavit of the amount of training he has had.

GRADING BASED UPON EXPERIENCE DESIRABLE

The industries must grade chemists in accordance with their experience. Men who have had the required training and who meet the other qualifications should be appointed first as junior chemists to serve at least two years before being promoted to the grade of assistant chemists, and at least three years' experience should be required before promotion to the grade of chemist. The title of chemist should mean something and should not be indiscriminately applied to all men, irrespective of their training and experience, who are employed in any way in connection with chemical activities. This or a similar system of grading chemists is essential if the profession is to receive the recognition which it deserves from the industries. The principle herein emphasized is in operation, I believe, in the Bureau of Chemistry, and in at least one laboratory connected with a chemical manufacturing plant. To be effective, however, any system must be general. Coöperation is needed among the employers of chemists to bring this about. No great achievement is possible in any department of human endeavor unless all the forces working toward a common end are coördinated and made one in purpose and action.

SIXTH NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES

"The Best Yet"—This phrase expressed the unanimous opinion of those who attended the Sixth National Exposition of Chemical Industries, at the Grand Central Palace, New York City, during the week September 20 to 25, 1920.

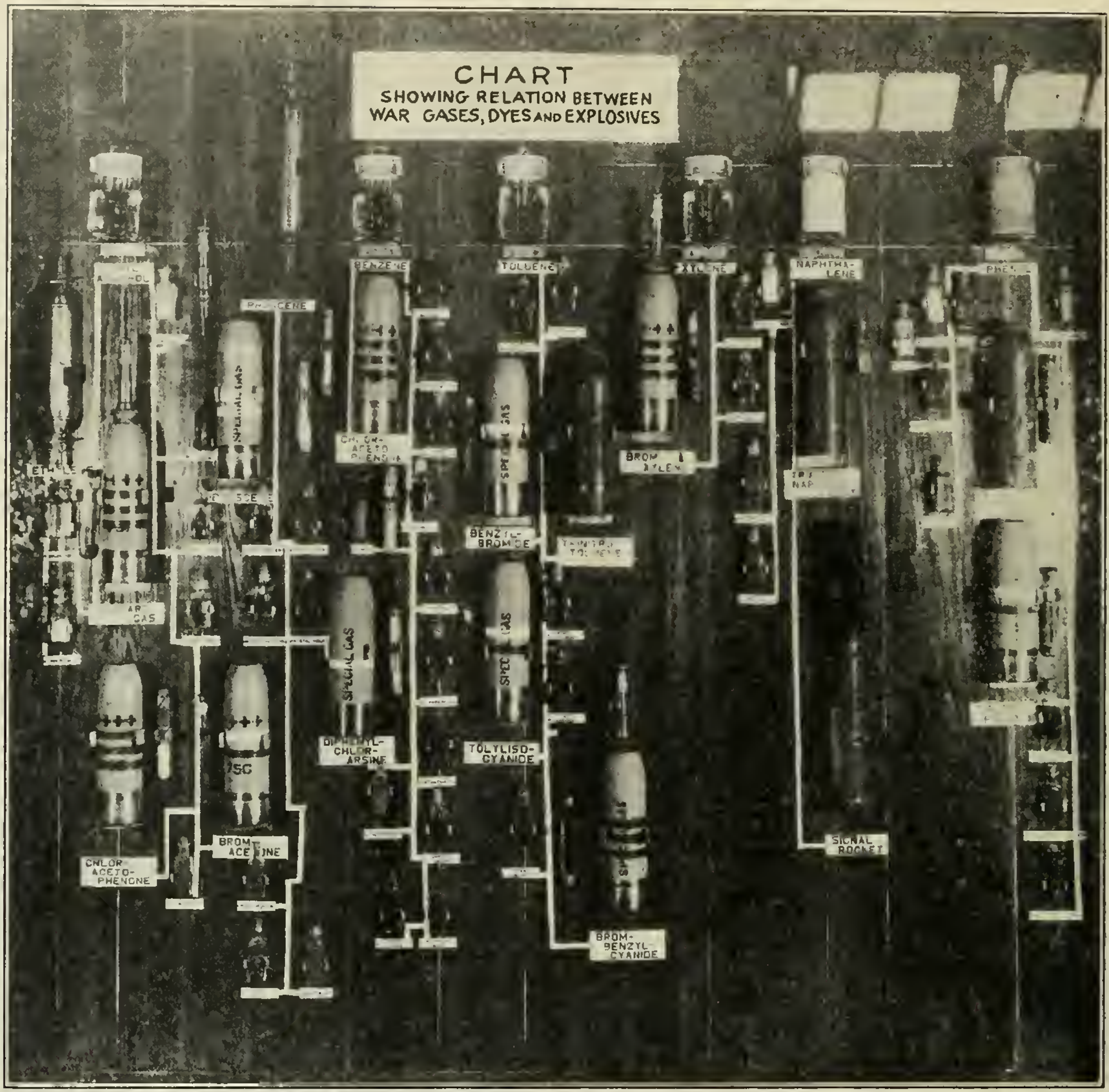
Many factors contributed to that enthusiastically favorable verdict. First and foremost was the total number of exhibitors, 457 as compared with a maximum of approximately 300 in previous years, a ratio which typifies the increasing magnitude and diversification of the American chemical industry. An attendance of over 125,000 thoughtful citizens clearly evidenced the constantly increasing popular interest in the work of our chemists. More thought had been given to the question of appropriate display, and more funds had been expended in transforming these thoughts into concrete form. So, too, the stenographer type of booth attendant, all too mistakenly prevalent in the past, was replaced by technically trained representatives of the exhibiting organizations, the result necessarily being an improved standard of "dope," to which in turn appreciative visitors listened with earnest attention. "The Show" is certainly a great educator.

The auditorium on the fourth floor was filled not only during the attractive "movies" depicting the intricacies of chemical industries, but also during the delivery of addresses at the symposiums on timely topics. Evidently the spoken word firmly holds its place in the Exposition program, despite the noise of nearby machinery in operation and the temptation to mingle with the crowd in the inspection of exhibits.

PUBLIC EDUCATION

If we were asked "What is the most striking outcome of the Sixth Exposition?" we would unhesitatingly answer—the education of the public on the subject of the intimate relation between dyes, synthetic medicinals, explosives, and toxic gases. There were a number of exhibits which brought this out clearly. The most effective were those of the Chemical Warfare Service, about which hung a constant throng, and of E. I. du Pont de Nemours & Co., where Dr. and Mrs. R. E. Rose, Dr. H. A. Lubs, Mr. E. W. Pierce, and Dr. West explained this relationship by means of formula models of the variety exhibited formerly only on the lecture tables of organic chemistry. It was a daring conception, and had we been asked to play the role of prophet, we would have predicted failure—

Models Showing Relationship between Dyes and Explosives



Chemical Warfare Service Chart Showing Relationship between Dyes and Explosives

but the public "ate it up." Dr. Rose used both his voice and his facile pen. The latter found expression in a fascinating booklet, "Molecules and Man," which was eagerly read.

The booklet distributed by the Texas Gulf Sulphur Company contained an interesting story of sulfur in the Southwest, but an equal number of pages was devoted to the physicochemical properties of sulfur. Highbrow stuff? Not at all, but a clear indication that the Exposition idea is developing a broader and sounder basis.

Another development of this year's Exposition was the increased use of models by those whose equipment is too bulky for display under booth restrictions of space. Among the many models were the working model of a rotary dryer exhibited by the Ruggles-Coles Engineering Co., a complete water softening outfit by the Permutit Co., an acid tank car by the General Chemical Co., a hydrochloric acid plant in operation at the General Ceramics Company's booth, and a new form of still for destructive distillation shown by the Fuel Products Corporation.

NATURAL RESOURCES

Accustomed thoughts of Florida as the home of citrus fruits and early truck gardens were displaced at the booth of Buckman, Pritchard and Co., where we gained for the first time an impression of Florida as a source of minerals. Titanium and zirconium ores are now being gathered in large quantities and of high purity from the sands of the East Coast.

The mineral exhibits from the South were not confined to Florida. The city of Knoxville again displayed the resources of those portions of Tennessee adjacent to that enterprising city; while the Southern Railway System and the Mobile and Ohio Railroad Co., through an elaborate exhibit prepared in coöperation with A. D. Little, Inc., and explained by talented representatives of that organization, showed a great field awaiting the chemist's hand for its development.

Natural resources again came to the fore in the group of Canadian exhibits. The Ontario Bureau of Mines, the Canadian Pacific Railway, and the Dominion Water Power Branch set forth these resources with attractive displays of charts and minerals, while the industries using the power at Shawinigan Falls showed the utilization of natural power in the conversion of raw material into useful chemical products.

Tremendous strides have been made in the number of applications of stellite since the first public inspection of that alloy afforded by Mr. Haynes just ten years ago during a journey of chemists to the San Francisco meeting of the AMERICAN CHEMICAL SOCIETY.

The Semet-Solvay Co., the Solvay Process Co., the General Chemical Co., the Barrett Co., and the National Aniline and Chemical Co., Inc., staged what was practically a joint exhibit, typical of the organic relationship into which these companies are now entering. Included in the exhibit was a living room completely outfitted with National dyes, from rugs, curtains, and clothing on the wax figures to the smallest toy among a child's playthings, and the food on the table.

The Newport Chemical Works, Inc., showing "Newport all the way" products on living models, failed to cover the subjects as completely as had been done in an adjacent aisle; nevertheless its exhibit was an attractive feature of the first floor.

At every turn one saw exhibits of dryers, evidencing the growth of the dye industry.

Peace application of a war development was easily recognizable in the number of exhibits of industrial gas masks. It is very clear that here a long-felt industrial need has been filled.

In the 1920 display of the Buffalo Foundry and Machine Co., each piece of apparatus represented either a new development or an improvement over apparatus shown at former Expositions.

NEW DEVELOPMENTS

Two very recently developed combinations of chemistry and art were shown. The Dow Chemical Company exhibited a number of oil paintings and water colors showing exterior and interior views of the plant. These were done by the British artist, Mr. A. H. Knighton Hammond, who seems to be a pioneer who has seen in a chemical plant fit subjects for the best work of an artist. On the other hand, the Eastman Kodak Company exhibited a series of paintings in which the application of chemical and physical principles gives a new power to the artist. For instance, an exquisite landscape scene, to the eye of the casual observer, when viewed through a ray filter became an equally artistic painting of the American national emblem. The artist, Mr. Charles Bittinger, in his choice of pigments had made application of the principle of invisible spectral differences of color and practically hidden one picture in the other, to be disclosed when viewed through properly filtered light.

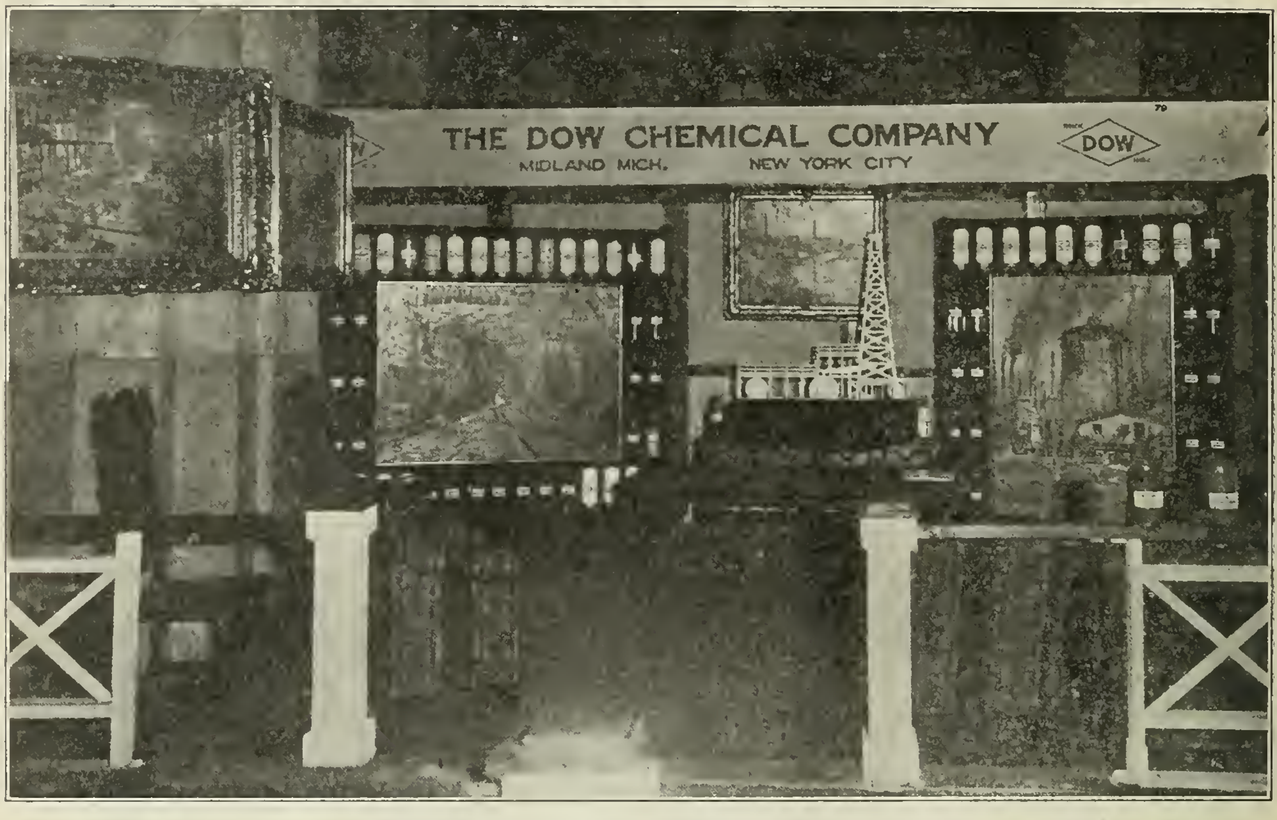
Franklin Filter Papers
A Grade For Every Purpose

The only unfortunate incident of the week was the masquerading of a lot of filter paper of indefinite but undoubted German origin. No marking indicative of German origin was visible, but in reply to direct questioning by two exhibitors the attendant at the booth admitted that the "Franklin Filter Paper," exhibited by the Rohde Laboratory Supply Co., was made in Germany.

This use of a good American's name to exploit a German product in a *National* Exposition of Chemical Industries bore out faithfully the prediction of the German engineer Herzog, who in 1918 in his book on "The Future of German Industrial Exports" wrote:

> "The German makeup is to be avoided wherever at all feasible out of regard for the rehabilitation of trade with formerly hostile countries. The German garb of manufactured articles must be put away."

SECTIONS OF THE BUFFALO FOUNDRY AND MACHINE COMPANY EXHIBIT



The Dow Chemical Company

[This extract is taken from the widely circulated translation of the book.] When the attention of the management was called to the display it was at once ordered removed. It was being shown in the booth of another exhibitor without the permission of the management.

FUTURE POLICY

This incident led to the formation of a definite future policy at the annual dinner given by the managers to the Advisory Committee on the last night of Exposition week. No exhibits of other than American origin will be permitted in the future except upon special authorization of the management and of the Advisory Committee. The Exposition will be held true to its original ideals, a setting forth to America of what her chemists are doing for American chemical independence.

It is a matter of regret to all that the Grand Central Palace is soon to be converted into an office building. It is fortunate, however, that there is available a great building, the Eighth Coast Artillery Armory, Jerome Avenue and Kingsbridge Road, easily accessible by the subway and elevated lines, and having much more space on one floor than was occupied by the entire Exposition just held. In this new location the "first floorers" will no longer hold the advantage over those who have had to be content with the higher tiers. Without this new building the Exposition would have had to be abandoned or a great many exhibitors excluded, for it was found that Madison Square Garden with all of its balconies the restaurant, etc., equaled in surface area only the first two floors of the Grand Central Palace, while the two next largest armories in the city contained less square feet for exhibition purposes than the main floor of the Palace.

"On with the Show!" Its stimulating effect upon the American chemical industry increases yearly, while its value as a public educator is inestimable.

OPENING ADDRESS

By Chas. H. Herty

Chairman of the Advisory Committee

The alchemist sought in secrecy his Philosopher's Stone with which to convert base metals into gold—the iatro (drug) chemist who followed the alchemist purposely shrouded his work in mystery, thinking that thereby he could practice best his fancied wizardry. The chemist of to-day, however, casts aside these false standards, takes the public frankly into his confidence and applies in his daily work common sense of the most thoroughgoing quality to every problem in which his talents can benefit humanity. The outward expression of this modern policy, in which America leads the world, is this annual display of the raw materials, the machinery, and the products of our chemical industries. That the story has its popular appeal is attested not only by the thousands who thoughtfully inspect these exhibits, but by the constantly increasing space given by our press to matters chemical.

It is a matter of special interest at the present time to note the amount of space devoted to preliminary accounts of this Exposition by the press of our neighbors in Central and South America. This is clearly indicative of a conviction on the part of the people of these countries that instead of looking to Germany as in the past, they must now look to America for the products of the chemical industries. This great field for export trade can be made permanently ours if we show constant good faith, high quality of products, attention to local desires, and care in shipments. These are better assets than the most elaborate programs of propaganda and subserviency to unrighteous political purposes which once permeated these markets.

PARTICIPATION OF RAILROADS

The most striking feature of the present Exposition is the reappearance of the exhibits by railroads of the natural resources along their lines. These displays locate for the chemist hitherto unknown sources of raw materials or set forth undeveloped resources which singly or in combination under the guiding sense of the chemists can be utilized to increase the national wealth. We are recovering from the blow dealt our industrial development by the absurd policy of the recent Railroad Administration which decreed a cessation of such exhibits. Fortunately, private ownership of railroads takes a more intelligent and progressive view of this important matter. Congratulations to those progressive railroads which have reinaugurated these exhibits! Their example will no doubt be followed by many others at the next Exposition.

AUTHORIZED CAPITAL AND EXPORTS

The possibilities for development of the chemical, drug, and dye industries are indicated by the authorized capital of the new companies organized during the past six years. These amounts, according to the *Journal of Commerce*, September 4, 1920, were as follows:

1915	$ 65,565,000
1916	99,244,000
1917	146,160,000
1918	73,403,000
1919	112,173,000
1920 (8 mo.)	167,992,000

In addition to supplying domestic needs, government statistics show that during the past fiscal year our exports of chemicals have been distributed in all of the principal countries of the world. The total value of these exports was $1,250,000,000. It is of particular interest that the products of our young dye industry were shipped in quantities whose valuation totaled $24,000,000.

NEED OF LEGISLATION

We must not be misled, however, by the foregoing figures. Those referring to capitalization represent *authorized* capital, not actual capital invested; they represent the confidence of American citizens in the great future of the American chemical industry. The magnitude of our dye exports is not indicative of a complete, self-sustained and well-rounded dye industry, but rather it is the concrete expression of the innate ability of the American to do on a large scale that which he has learned to do. Many gaps are yet to be filled before that industry is complete. We must candidly face the fact that during the past six months there has been a decided slowing up in our chemical development. The execution of many completed plans for expansion has been postponed because actual capital has been timid. Why? Because Congress adjourned in June last without enacting into law any one of those several measures whose purpose was the protection and safeguarding of those industries which had sprung into being to fill the nation's obvious needs as affected by the exigencies of war.

A damaging blow has been dealt by our legislative representatives through their inaction. It is not difficult to imagine the satisfaction which this situation gives to those who formerly boasted of their domination of us in matters chemical and who now openly avow their determination to recover their lost markets. To all who have read the revelations of the base use to which that former domination was put through corruption of our industrial life and through the establishment of a complete system of espionage which for a long time in a critical period misled public opinion and crippled our effectiveness by sabotage made easy, this prospect of a recovery of markets can be looked upon only as an impending national curse. The warding off of this peril, however, is not difficult. The case has been fully presented to the Congress, a great majority opinion, absolutely non-partisan in its character, has been developed, the House of Representatives has already acted favorably, but the Senate has failed to act. Public opinion should make itself felt—for the vital interests of the public are at stake—and insist that at the approaching winter session of the Congress this legislation be completed. If this be done, I prophesy a new era in our chemical development, which will make the successes of the past five years pale into insignificance and guarantee forever the economic independence of this country in all lines of chemical industry.

These thoughts apply particularly to our dye industry. Here much has been accomplished, progress has been phenomenal, yet much remains to be done. We cannot afford to delay the completion of this industry, for it is too intimately bound up with a vast number of our other industries and stands too closely knit with that latest development of warfare upon which our country's future safety may depend. It is a short-sighted and ill-informed American who is impatient and complains because our dye industry is not yet completely rounded out.

THE FOOD OF THE NATION

Of the three essential constituents of plant food, phosphorus, nitrogen, and potassium, nature has abundantly blessed us with phosphorus in the form of the great phosphate deposits of our southeastern and northwestern states, but our efforts to provide domestic sources of nitrogen and potassium have proved ineffectual.

Whatever mistakes may have been made in our past efforts on fixation of atmospheric nitrogen, that industry must be established. The use of nitrogenous compounds in peace as a fertilizer and in war as an explosive points clearly to the fact that we cannot afford to continue dependent for such supplies on ship transport from outside our borders. The submarine has demonstrated its ability to destroy selected ship-commerce, and submarines can ply in the Pacific as well as in the Atlantic Ocean.

In potash matters we have played a losing game. In the false hope of a return to the cheap foreign potash of pre-war days, we have withheld that encouragement and stimulation of our domestic potash industry which would have assured the full development of our own resources, and now we are paying tribute to the extent of millions on millions of dollars. Where thousands of dollars have been spent on research on potash and its development, millions could have been spent whose total amount would not be a tithe of the millions we seem destined to pay as tribute unless our policies be quickly changed.

INDUSTRIAL RESEARCH

In other lines, however, the progress of industrial research has been phenomenal. Conservative estimates place the amount to be expended this year on industrial research laboratories, personnel, housing, and equipment, at $25,000,000. Evidently our industries as a whole are passing out of the empirical stage and are realizing that the greatest progress is to be made through scientific development and accurate control. On the journey of the AMERICAN CHEMICAL SOCIETY to San Francisco in 1910 I was shown a new alloy which at that time had found no industrial application. To-day, however, that alloy and similar ones have increased the output of our machine shops threefold, because with the same number of men and the same amount of equipment, machines can be run three times as fast. It is not difficult to understand how great a role this one development played in the rapid equipment of our armies during the war.

And this bit of history suggests the possibility of overcoming the present inefficiency of labor through research on improved methods of operation of all lines of industry. Increased production through greater utilization of chemistry is a phrase which America should take deep to heart.

ALCOHOL EXCISE TAX

In this survey of present-day conditions, may I direct your attention to one anomalous situation? Alcohol is one of the most important reagents used by chemists. Congress recognized this fact in the enactment of the National Prohibition Act, which, while providing for the abolition of alcohol as a beverage, nevertheless made distinct provision for stimulating the production and facilitating the distribution of tax-free alcohol as a chemical reagent. And yet a recently enacted law in the state of New York, the very heart of chemistry in America, imposes an excise tax of thirty cents per gallon on that alcohol which the Congress provided should be, from the federal standpoint, tax-free. No other chemical reagent bears a similar tax. That law constitutes a hardship upon our industries and our universities, and it is sincerely to be hoped that the State Assembly will promptly repeal such a crippling and unjustifiable measure.

COÖPERATION WITH THE CHEMICAL WARFARE SERVICE

Now let me make an announcement of greatest import to our country. The Congress, during its last session, in framing the Army Reorganization bill, constituted by an overwhelming vote the Chemical Warfare Service a separate and independent unit of the Army, in the conviction that it could thus be developed most effectively. At its head the President has placed that brilliant soldier, Brigadier General Amos A. Fries, who led the field forces of that Service with the American Expeditionary Forces. Upon invitation of General Fries, the American Chemical Society has pledged the active aid of its 15,000 civilian members in the successful development and prosecution of the work of the Chemical Warfare Service. The connecting link between that army of 15,000 silent workers in the laboratories of America and the official service in the War Department will be a committee consisting of:

W. D. Bancroft, Dept. of Chemistry, Cornell University, Ithaca, N. Y.
E. P. Kohler, Dept. of Organic Chemistry, Harvard University, Cambridge, Mass.
A. B. Lamb, Dept. of Chemistry, Harvard University, Cambridge, Mass.
R. C. Tolman, Fixed Nitrogen Research Laboratory, Washington, D C.
F. M. Dorsey, Nela Research Laboratory, Cleveland, Ohio
W. K. Lewis, Dept. of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Mass.
L. T. Sutherland, Sutherland Industrial Research Co., New York City
Bradley Dewey, Dewey & Almy Chemical Co., Cambridge, Mass.
L. C. Jones, National Aniline & Chemical Co., Inc., New York City
C. L. Reese, E. I. du Pont de Nemours & Co., Wilmington, Del.
W. H. Walker, Division of Industrial Coöperation and Research, Massachusetts Institute of Technology, Cambridge, Mass.
Reid Hunt, Dept. of Pharmacology, Harvard Medical School, Boston, Mass.
A. S. Loevenhart, Dept of Pharmacology, University of Wisconsin, Madison, Wis.
Julius Stieglitz, Dept. of Chemistry, University of Chicago, Chicago, Ill.
Chas. H. Herty, Journal of Industrial and Engineering Chemistry, New York City.

In this list are men whose brilliant work accomplished such wonders in the manufacture of gas masks for defense and gases for offense. The laboratories of our universities and of our industries are both represented So, too, are the representatives of our dye plants included. I count it the highest honor of my life that I am to be permitted to serve my country through the chairmanship of this committee. I feel no hesitation in pledging to General Fries not only the united coöperation of the chemistry personnel of the country but also that of our industrial chemical plants.

Chemical warfare has come to stay. The effectiveness of gas in warfare has been proved by the fact that one-third of the total hospital cases in our Army were due to gas; its inhumanity has not proved itself in the light of history, for of this third our medical records show that the very great majority completely recovered, a far greater proportion than of those who were wounded by shot and shell. The fear of tuberculosis development among our gassed wounded has been proved baseless.

This happy outcome as to recovery removes in no wise the stigma which will always attach to Germany as the introducer of gas warfare. The heinousness of her offense against civilization lay in the breach of good faith in international agreement that gases would not be used in warfare. By this treacherous initiative she was enabled to destroy thousands of men of those nations who in good faith had provided no means of defense against such a means of warfare. America proposes to see to it that should her armies ever be called upon to take the field again, which God grant may never come to pass, those armies will be furnished immediately with the best means of defense which American ingenuity can in the meanwhile devise, and with an abundance of gases which will be immediately forthcoming, limited only by the resources of our land. These steps will constitute no tax upon our people in time of peace, but preparedness along this line of warfare will be thorough.

The *New York Times* of to-day discusses the subject of chemical warfare in an editorial entitled "A Chemists' War." In this editorial there are two noteworthy errors; one as to fact, the other as to national policy as I see it.

As to the question of fact, the *Times* states: "It was difficult to interest Congress in the establishment of a permanent Chemical Warfare Service Bureau, to be attached to the War Department." The fact is, as the public records show, there was no difficulty in convincing Congress on this point. The difficulty lay, however, in the objections by the Secretary of War and the Chief of Staff in statements made before the Senate Committee on Military Affairs. The action of Congress in establishing the Chemical Warfare Service as a separate unit of the Army was taken in spite of these objections.

As to the question of policy, the *Times* at the conclusion of its editorial says:

> It cannot be impressed upon civilized peoples too much that a chemists' war would be incalculably more disastrous to the nations engaged in it than the struggle of 1914–18. The American people must ask themselves whether they can afford to disregard the conviction of the thirty-nine countries now forming the League of Nations that it offers the best safeguards against the horrors and waste of modern war.

This recalls an interesting colloquy which took place between General March and Senators Chamberlain and Sutherland in the Hearings on S 2715, pages 95 and 96.

GENERAL MARCH—Here they are, sir. That is my best thought on that subject. If the provision in the so-called league of nations, which prohibits the use of poison gas is carried out, all of that will disappear.

SENATOR CHAMBERLAIN—If the provisions of the league of nations were carried out, we would not need any Army.

GENERAL MARCH—I do not see that.

SENATOR CHAMBERLAIN—We are going to have peace; the millenium is going to be here. I have not any idea it will all be carried out.

SENATOR SUTHERLAND—We have already had some agreements about humane warfare, but none of them were carried out.

GENERAL MARCH—That is true, but this provision specifically says that, the use of poison gas having been prohibited, Germany is forbidden to import into her territory any of the elements which make for poison gas or liquid gas, which is forbidden, the thought being that Germany was the only nation in the world that would start any such thing.

SENATOR CHAMBERLAIN—Well, I think there are others, if they had had the chance.

The provision in the Peace Treaty by which, according to General March, "Germany is forbidden to import into her territory any of the elements which make for poison gas or liquid gas" doubtless gives to the Germans the same sense of despair that America would feel if, at the conclusion of an unsuccessful war, it were forbidden "to import" cotton for use in the manufacture of guncotton or iron ores for making steel for guns.

COÖPERATION IN CITY DISASTERS

Coöperation should, however, not be confined to national affairs. Within the last few days a terrible disaster has occurred in New York City. As a result of the work of perverted minds, many citizens were instantly killed and many more horribly mangled. The evidence which would determine the cause of such a disaster and trace its perpetrators is largely chemical. The time to utilize the chemist in such a situation is immediately after the disaster takes place. In the New York Section of the AMERICAN CHEMICAL SOCIETY more than two thousand chemists are numbered, among them men who are specialists in explosives, in metallurgy, and in cement. No one of these men, no matter how prominent or how immersed in his own laboratory, could as a patriotic citizen decline an invitation to serve on a committee advisory to the city authorities in such cases of great disaster. Provided with official passes through the police lines they could be of invaluable service through their special knowledge and acumen. For such public service they would desire no pay. There is a civic asset here which is lying neglected and which can be quickened into dynamic aid by a simple request from the municipal authorities.

COÖPERATION IN THE ALLEVIATION OF HUMAN SUFFERING

Fortunately the future energies of our chemists are not to be confined to increasing the wealth of the country and providing means for its defense. There is a higher goal ahead for American chemistry, it is the alleviation of human suffering. The normal, healthy, vigorous human being is a mass of chemical reactions which can be called normal. When these become abnormal we speak of disease, and disease entails suffering. About many of these subtle changes we know little. In our blind efforts to restore normality we try this and that drug, sometimes with success, many times with utter failure. Eminent authorities inform me that of the many synthetic medicinals sold by Germany to this country only from three to five per cent have proved of real value. We know in general terms the results from the use of drugs, but of the fundamental reactions induced by their use we know but little. These changes in the body effected by drugs are chemical changes, but in their study in the past the chemist has played but a minor part, and we have been content to continue the "cut and try" process in our efforts to heal. It is now proposed to give the chemist the leadership in this his own line of research. But he is not qualified to work out the problem alone, for the conditions are very complex. He must be associated with the pharmacologist and the experimental biologist With the focusing of these three types of mind upon the problems of health, under conditions of constant association and adequate experimental facilities, real progress can be made, even though slowly, in the alleviation of suffering. It is a task worthy of the best efforts of our very ablest men. Funds will be required for its prosecution. Fortunately the Chemical Foundation, Inc., which under its charter must spend all above six per cent of its earnings on scientific research, sees in this direction the channel through which it can best perform its mission. It has therefore pledged a sufficient amount for immediate use to insure the inauguration of this work. It is confidently believed that as the work takes definite shape and progresses it will make its own appeal to those generous Americans who have never yet failed to respond to the cause of humanity when convinced that the right way to aid has been shown them.

PROGRESS OF THE AMERICAN COAL-TAR CHEMICAL INDUSTRY DURING 1919

By Grinnell Jones

Chief Chemist of the U. S. Tariff Commission

A year ago, the annual census of dyes and other coal-tar chemicals, prepared by the Tariff Commission, was published on June 11. This year it has been unavoidably delayed owing to the fact that a general census of manufactures of all kinds is being taken by the Bureau of the Census. In order to avoid having two different branches of the Government each send its questionnaire to every manufacturer, it was arranged that the collection of the reports should be undertaken by the Census Bureau, whereas the tabulation and interpretation of the reports on dyes and coal-tar chemicals would be done by the Tariff Commission. The Census Bureau has secured reports from a number of small manufacturers who were unknown to us. However, the collection of the reports has been much delayed by the coöperative arrangement, and the reports of over a dozen firms have not yet been turned over to the Tariff Commission. However, the missing reports are all believed to be of small firms. I am confident that our records are sufficiently complete to show clearly the progress made during the year, but any figures given are subject to revision upward.

The Geological Survey has recently reported that the production of by-product coke and the by-products obtained therefrom during the year 1919 shows a slight decrease, as compared with 1918. This was due to labor troubles in the steel and coal-mining industries and to railroad congestion. There appears to have been a small decrease in the amount of tar distilled and a large decrease in the output of pure benzene, and especially of pure toluene. This means that a much larger proportion of the output was sold as mixtures for solvent purposes or as motor spirit, instead of in the purified condition. Of more significance in considering the future of the coal-tar chemical industry is the fact that the productive capacity of the by-product coke ovens in the United States increased 17.2 per cent during 1919. There is no question that, with the possible exception of anthracene, adequate supplies of the fundamental raw materials of coal-tar origin will be available from American sources for the growth of the industry.

THE PROBLEM OF ANTHRACENE SUPPLY

In the case of anthracene considerable progress has been made during the past year, but the problem of securing adequate supplies is still unsolved. In 1918, the anthracene content of the crude anthracene produced was about a quarter million pounds, but very little of this was refined. In 1919 the output of crude anthracene was about three times the 1918 record, and a much larger fraction of it was refined. Although this shows great and encouraging progress, a much greater increase in output must be secured before there will be enough American anthracene available to supply the American demand for alizarin and vat dyes. It may be roughly estimated that the 1919 production of crude anthracene contained less than one-fifth of the amount of anthracene which would be required to supply the American needs. The difficulty is not primarily an actual lack of anthracene in the tar or purely technical difficulties in its recovery, but rather the fact that its removal leaves the pitch so hard that it does not find a ready market under American conditions. In England and Germany large amounts of hard pitch were used for the briqueting of coal dust and coke breeze, but this industry is very little developed in the United States. Any method of recovering anthracene which seriously disturbs the marketability of the other larger fractions of the tar, especially the pitch, would make the anthracene so expensive that the dyes derived therefrom could not be made on a competitive basis.

This problem of securing supplies of anthracene adequate in amount and at a cost which is not prohibitive is perhaps the most important and most fundamental problem still awaiting solution in this industry. Whether it will be solved by the tar distillers or by the development of a synthetic process for making anthracene or anthraquinone cannot be determined at the present time. Active work along both lines is now under way and the progress already made is encouraging.

THE PRODUCTION OF INTERMEDIATES

As was to have been expected, there was a large decrease in the output of several intermediates needed primarily for explosives. This is most noticeable in the case of phenol, which showed an enormous production—106,000,000 lbs.—in 1918, but fell to less than 1,500,000 lbs. in 1919, nearly all of this being obtained from coal tar. A less conspicuous case is the decrease in the output of monochlorobenzene from 20,500,000 lbs., in 1918, to a little more than 4,000,000 lbs. in 1919. There was also a considerable decrease in the output of several intermediates required for making dyes used for army uniforms; for example, there was a 25 per cent decrease in the output of *m*-toluylenediamine, which was used for making a khaki dye for cotton uniforms, and a 90 per cent decrease in *m*-nitroaniline, which was used for making a khaki dye for wool uniforms. It is my purpose to-day to give some typical examples of the progress of the American coal-tar chemical industry under peace conditions.

A comparison of the intermediates produced in 1918 and 1919 shows a considerable increase in the number of intermediates and substantial increase in amount in many cases. In 1919 there were about 225 different intermediates produced, against about 140 in 1918. The new intermediates are, of course, comparatively difficult to make, but were needed for dyes and medicinals of the better class. Among these new intermediates may be mentioned bromobenzene, dibenzylaniline, dichloroaniline, nine new sulfonic acid derivatives of naphthol or naphthylamine, β-oxynaphthoic acid, and five new anthraquinone derivatives.

As a rule, the intermediates for which there is the largest demand, and whose manufacture had been well established by 1918, show comparatively little change in 1919. Thus, nitrobenzene gained 11 per cent, the 1919 output amounting to about 42,500,000 lbs.; the output of aniline was about 24,500,000 lbs., a gain of 1 per cent; *p*-nitroaniline, with an output of about 1,300,000 lbs., lost 1 per cent; and β-naphthol, with an output of about 5,000,000 lbs., dropped 6 per cent. The output of H acid increased from a little less than 3,000,000 lbs., in 1918, to about 4,000,000 in 1919; on the other hand, the output of dimethylaniline fell off about 15 per cent, amounting to 3,500,000 lbs.

There are many notable increases in the output of individual intermediates, especially noticeable in the case of those derived from toluene or from anthracene. The output of U. S. P. benzoic acid increased from about 173,000 lbs., in 1918, to over 600,000 lbs. in 1919, with a drop in valuation from $3.07 to 74 cents per lb. *o*-Toluidine increased from 639,000 lbs. to a little over 1,000,000 lbs., and *p*-toluidine from about 200,000 lbs. to over 575,000 lbs., with a drop in valuation per pound to nearly half the 1918 figures. The general increase in the output of intermediates derived from toluene is, of course, due to the relaxation of the restriction on the use of toluene during war times.

There are also many examples of a big increase in the production of intermediates which are difficult to make, but are required for dyes of the best quality. A good example of this kind is amidonaphthol sulfonic acid, 2:8:6 (gamma acid), which was made in 1918 by a single firm, but in 1919 by five firms, with an output of over 155,000 lbs. valued at $667,000, which is many times the 1918 output. These five firms used this gamma acid to make nearly a half million pounds of Oxamine Black—an important direct black which can be developed. Moreover, gamma acid also went into Diamine Fast Red F, Neutral Gray G, and Columbia Black F B—all of them important direct cotton dyes of faster type.

Other intermediates, whose output increased substantially, include metanilic acid, with an output during 1919 of 450,000 lbs.; ethybenzylaniline, which served for the manufacture of Acid Violet; Michler's ketone (280,000 lbs.) used mainly for the important dye Auramine; thiocarbanilide (2,250,000 lbs.) used as an accelerator for vulcanizing rubber; naphthylamine sulfonic acids 1:5 and 1:8; and amidonaphthol sulfonic acid 1:2:4 (about 900,000 lbs.), important naphthaline derivatives.

The progress among the anthracene derivatives is of especial interest. Here, unfortunately, definite figures cannot be given without revealing confidential information. In 1919, there were ten intermediates derived from anthracene, against only five in 1918. The output of anthraquinone, which is the most important because it serves as raw material for the manufacture of nearly all other intermediates derived from anthracene, was about ten times as great in 1919 as in 1918.

THE PRODUCTION OF DYES

The total output of all dyes increased about 8 per cent over 1918, or to a little more than 63,000,000 lbs., valued at about $67,000,000. The average value per pound was $1.07, which is just the same as shown by the 1918 census. The average quality of the dyes has, however, improved considerably, owing to a partial replacement of many of the cheaper dyes by others of a more satisfactory character. The consumer, accordingly, received better value for his money in 1919 than in 1918.

The production of basic dyes for 1919 was over 4,000,000 lbs., an increase of more than 1,000,000 lbs., as compared with 1918. The production of Magenta, Victoria Blue, Malachite Green, and Bismarck Brown more than doubled, while Auramine nearly trebled. There has been a conspicuous increase in the production of Rhodamine B.

The production of direct dyes was about 14,500,000 lbs., an increase of 2,000,000 lbs., as compared with 1918. About half of this total was direct Deep Black E W. Conspicuous changes include large increases in the output of Chrysophenine, Primuline, Oxamine Black, Diamine Rose, and the first appearance of Diamine Fast Red F.

The production of mordant dyes during 1919 was over 3,100,000 lbs., which is about 2,300,000 lbs. less than the output of mordant dyes in 1918. This decrease is due principally to a diminished production of Alizarin Yellow G G and R of more than 2,000,000 lbs. Mordant dyes available in 1919 in considerable, although inadequate, amounts, included alizarin, Alizarin Saphirole, and other alizarin derivatives, as well as a considerable number of fast mordant dyes for wool dyeing and mordant printing.

The production of acid dyes for 1919 was over 14,000,000 lbs., an increase of about 6,000,000 lbs. over 1918.

The production of indigo, 20 per cent paste, reached 8,863,824 lbs., valued at $5,233,719. This exceeded the 1914 importation

Chemical Warfare Service Exhibit

by 356,465 lbs., and the 1918 production by 5,779,936 lbs. Several indigo derivatives were placed on the market. Four other vat dyes were made on a commercial scale during 1919, but the output was only a small fraction of the pre-war consumption. However, fundamental progress has been made in this important field.

The total production of sulfur colors for 1919 was over 17,000,000 lbs. This was about 6,000,000 lbs. less than that for 1918. This was largely due to a decrease of about 8,000,000 lbs. of sulfur olive and khaki dyes required in the war period for cotton uniform cloths. Sulfur black production in 1919 (14,250,000 lbs.) was about 2,000,000 lbs. more than that for 1918.

COAL-TAR MEDICINALS AND PHOTOGRAPHIC DEVELOPERS

Among the coal-tar medicinals there has been a substantial increase in the output of many items already well established in 1918, including aspirin, acetphenetidin, arsphenamine, guaiacol, and methyl salicylate. Moreover, a considerable number of new products have been introduced on a small scale.

In the case of photographic developers of coal-tar origin, there was a decrease of 30 per cent in the output of hydroquinol—to about 200,000 lbs. valued at nearly half a million dollars. On the other hand, the output of metol increased more than five times—to nearly 60,000 lbs., and *p*-aminophenol increased about 7 per cent, or to over 130,000 lbs.

The many difficult problems in readjustment from war conditions to peace conditions have been met with encouraging success. The achievements of American chemists in these industries furnish an excellent basis for optimism as to the future.

REORGANIZATION OF THE CHEMICAL WARFARE POST OF THE AMERICAN LEGION

Major L. T. Sutherland presided at the reorganization meeting of the Chemical Warfare Post of the American Legion, and introduced Brigadier General Amos A. Fries, the present head of the Chemical Warfare Service, who outlined the plans of the Service and made an earnest plea for the coöperation of civilian chemists with the military organization.

General Fries pointed out the difficulty of educating, in times of peace, to the necessity of preparing for chemical warfare, both in the offensive and defensive sense. He cited statistics recently given out by the Army to the effect that three out of every ten casualties in the World War were due to gas and one-third of the wounds inflicted were also due to gas attacks.

General Fries voiced the appreciation of the Chemical Warfare Service for the aid that has been given by civilian chemists to obtain proper recognition for the Service.

Civilian chemists and particularly former officers of the Chemical Warfare Service will be called upon frequently, said General Fries, to aid in the work of the Army, and a reserve corps will be organized in the near future through which active coöperation with civilian chemists can be established. National guard units as well as regular army divisions will be trained in gas warfare.

Following remarks, voicing the willingness of civilian chemists, and particularly former service men, to coöperate with General Fries in every way, by Colonels Burrell, Bogert, and

Walker, the election of officers for the Post was held. The new officers are: Commander, Major L. T. Sutherland; Vice Commander, Lt. Col. Mayo Smith; Adjutant, Capt. E. Caldwell; Treasurer, Major Fred C. Zinnser; Members of Executive Board: Colonels W. H. Walker, F. M. Dorsey, Bradley Dewey, R. F. Bacon, G. A. Burrell, and W. S. Bacon.

Before adjournment the Post passed a resolution to be sent to Congress endorsing the dye bill and urging its speedy passage.

All former members of the Chemical Warfare Service are urged to affiliate themselves with this Post, and to send the necessary dues to the treasurer, Major Fred C. Zinnser, Hastings-on-Hudson, N. Y.

ABSTRACTS FROM THE MEETINGS

OPENING MEETING

The opening address, by the chairman of the Advisory Committee, is printed on pages 956 to 959

Dr. Chas. L. Reese, president of the Manufacturing Chemists' Association of America, pointed out the ways in which the Exposition had furthered coöperation between the producer of chemicals and the manufacturer of apparatus. American manufacturers, according to Dr. Reese, are furnishing better glassware and porcelain than ever was obtainable from foreign sources. There is still work to be done; present needs include improved autoclaves for use in the dye industry, and better standardization of laboratory apparatus. A committee of chemists is coöperating with the manufacturers in an effort to eliminate a large number of pieces and have the remainder of the apparatus conform to the specifications of the Bureau of Standards.

Following Dr. Reese, Col. J. S. Dennis, assistant to the president of the Canadian Pacific Railway Co., spoke as the representative of our Canadian neighbors. He said that Canada's future development depends upon increasing her population and developing those natural resources which can better Canada's financial position only through effective expansion.

In a discussion of the "Problems Confronting the American Exporter," Erasmus Hopkins, of Gaston, Williams and Wigmore, Inc., pointed out the weaknesses of American foreign selling methods, as compared with those of the English and German exporter. The American manufacturer must realize that, in foreign even more than in domestic trade, shipments must meet requirements as to quality and time of delivery. Materials should be packed in units conforming to the system of the country to which they are to be sent. The manufacturer must coöperate with the exporting house in regard to the financial side of its foreign business.

FUEL ECONOMY SYMPOSIUM

In opening the Fuel Economy Symposium, Chairman R. C. Beadle, managing editor of *Combustion*, said in part:

> The Chemical Exposition has this year for the first time recognized the tremendous importance of all those things which go to make for better efficiency, by setting aside a day of this week when matters may be discussed which relate to that brother of the chemical engineer, known as the combustion engineer, in its fuel economy conference, discussing carefully with eminent authorities all phases of industrial activity that relate in any way to economy in the production of that underlying force which drives the wheels of all our industries.

Mr. W. O. Rankin, of the Quigley Furnace Specialties Company, stated that powdered coal has met the demand for a highly efficient fuel in the metallurgical industries, and is now coming into the field in power plant operation. With furnaces of proper design, a 20 to 40 per cent increase in efficiency and a fuel consumption reduction of 25 to 60 per cent are easily possible.

F F. Uehling, of the Uehling Instrument Company, stated that "no matter how fuel is burned, and no matter what fuel are used, whether solid, powdered, liquid or gaseous, the biggest loss is always due to the heat energy wasted up the chimney." The loss depends upon three factors: namely, excess air in the products of combustion, the temperature of the products of combustion, and the amount of unconsumed fuel in the products of combustion. These three points, respectively, may be controlled by the continuous automatic determination of CO_2, the use of an ordinary flue-gas thermometer, and the determination of CO.

In modern heating systems using oil as a circulating medium, said Alexander Mackechnie of the Parks-Cramer Company, difficulty on account of carbonization of the oil has been eliminated. The method is not a substitute for steam heating, but is adaptable for temperatures to which dry saturated steam cannot reach.

W. B. Chapman, of the Chapman Engineering Company, showed a large and complete series of lantern slides illustrating the development of the gas producer up to the modern type, with its important accessories in the line of gas-cleaning and regulating devices. The present-day tendency is toward simplicity of design, the use of accessories which will show the operator just what he is doing, and the employment of better men in charge of the process.

F. L. Reisman, also of the Quigley Furnace Specialties Company, discussed the application of plastic high temperature cement in the place of fire clay. The extra initial cost of the cement is more than balanced by the increased life of the furnace. For instance, a wall which, laid in fire clay, would last three months can be made to last three and a half years by the use of the cement.

In his paper on "Preventing Conduction and Radiation Heat Waste," S. L. Barnes, of the Armstrong Cork Company, emphasized the necessity of reducing the heat losses which occur through conduction and radiation from boiler settings, furnaces, kilns, etc. The reduction of heat loss by insulation increases the capacity of the equipment without increase in fuel consumption, makes temperatures more constant and uniform throughout the apparatus, decreases the time required to bring equipment to working temperature, lengthens the life of refractories by eliminating the necessity for overheating, and provides more comfortable working conditions for operatives.

W. R. Van Nortwick, of the Roto Company, pointed out the loss in boiler efficiency due to soot and boiler scale. In one case cited, with a new and perfectly clean horizontal tube boiler of 600 h. p. capacity, the uptake temperatures increased 100° in four days, an increase in fuel consumption of 5 per cent, due to failure to blow the soot from the tubes. Service tests indicate that boilers blown every 6 hrs. show an increased efficiency of 4 to 5 per cent over those blown every 24 hrs. Mr. Van Nortwick advocated mechanical removal of boiler scale in preference to the use of boiler compounds, as more practical and more economical.

Conrad Dressler, of the American Dressler Tunnel Kilns, Inc., outlined the process employed in the Dressler kiln, and pointed out the various ways in which the kiln construction contributed to fuel economy.

INDUSTRIAL MANAGEMENT SYMPOSIUM

Harrington Emerson, first speaker in the Industrial Management Symposium, emphasized the value of ultra analysis of costs in factory operations in order that concentration of supervision may be effectually focused on those items showing the widest deviations from standard efficiency. He brought out the point that the cost accountant needs the coöperation of the technical man who knows the operation of a particular plant

Mr. Emerson said that the chemical industries operate with the fundamental elements of cost accounting, namely, materials, personnel, and equipment, and that it is probable that the chemical industries set up standard costs more rigidly than most other industries.

In discussing the part played by research in industrial conservation, H. E. Howe, of the National Research Council, gave numerous concrete illustrations of increased economic production effected through the application of scientific principles. A striking illustration in point is the results achieved through the coöperation of engineers, chemists, physicists, and metallurgists on the problem of more efficient illumination of industrial plants. In conclusion Mr. Howe said:

> While much has been accomplished, it is apparent that there is much more yet to be done and scientists are continually endeavoring to have the public at large understand its pressing needs and to have industry avail itself of what science is now able to offer. Industry must support science in its effort to establish an increasing number of fundamental principles which can be applied to the further solution of industrial problems. There are a number of the natural sciences which have not been introduced to industry in the same way as has chemistry. Oftentimes industry is unfortunate in placing its problem before a particular science when another is better able to be of real assistance. In the past too often the sciences themselves have remained apart and have not contributed each to the other's work in as great a degree as is desirable. Wherever sciences have been cross-fertilized, the results have been remarkable and the achievements to be accredited to physical chemistry to-day are an illustration of the point I would make. * * * *
>
> Often when such arguments as I have presented are laid before a man in the industry he assents as to their soundness and may often appear bored at a repetition of an old story, but in too many cases he remains unconvinced and feels that his own industry is so peculiar that no lessons can be drawn from the experience of others and that he is doing so well that the assistance of science is not required. It is in a change of this attitude that we are particularly interested, and our effort is to change a passive agreement with our viewpoint into an active application of the principles which we know from experience to be sound.

The report of Grinnell Jones, chief chemist of the U. S. Tariff Commission, upon the "Progress of the American Coal-tar Chemical Industry during 1919" is printed on pages 959 to 961.

MATERIALS HANDLING SYMPOSIUM

In his opening address, Roy V. Wright, editor of the "Material Handling Cyclopedia," declared that the present problem of speeding up the transportation of raw materials and finished articles is dependent upon the improvement of facilities for handling at freight terminals.

The next speaker, J. H. Leonard, editor of *Freight and Terminal Engineering*, emphasized the fact that the "proper handling of materials is an engineering function from beginning to end," and that "every branch of engineering science must aid in the solution of the problem."

Ramsey W. Scott, of the Technical Advisory Corporation, likewise discussed transportation facilities, from the standpoint of handling the country's food supply.

Willis T. Spivey, material handling engineer, asserted that "the keynote of successful conveyor installation is *right application*," and "that no type of production equipment depends more upon surrounding plant conditions." The sales-engineer must therefore carefully analyze the problem, including the existing routing methods with their probable changes, a comparison of the cost in time and labor of the present handling method with that after the proposed installation is made, special conditions which may effect its economical operation, and probable plant changes or additions.

Everett W. Morgan, of the Pneumatic Scale Corporation, displayed and discussed the advantages of a metal shipping container. As one illustration, he quoted from the Underwood resolution before the Senate last spring, to the effect that "the wooden packing cases and containers made of soft wood" (in the United States in 1919) "consumed enough material to manufacture 4,000,000 tons of paper, or, in round numbers, double the quantity manufactured by all the newsprint mills of Canada and the United States combined." The use of steel containers would release this enormous amount of material for the paper industry.

CHEMICAL ENGINEERING SYMPOSIUM

The Chemical Engineering Symposium was conducted by the American Institute of Chemical Engineers. Chairman David Wesson pointed out the every-day duties of the chemical engineer. As a citizen, it is his duty, Dr. Wesson said, to show his interest in various patent laws and tariff bills now pending, by giving to the congressman the benefit of his knowledge and experience.

Thomas W. Pritchard, of the Fuel Products Corporation, presented a new method by which destructive distillation may be carried on under more definite temperature control, thus reducing the time of operation by one-third, and at the same time improving yield and quality of product. In brief, the change consists in conducting the uncondensed vapors from the condenser through a thirty-eight blower and superheater back through the retort, thus distributing the heat units throughout the mass, as well as sweeping out the vapors formed.

Robert G. Guthrie, of the Widney Test Laboratories, declared that the question of the relation of recoverance to fatigue is of vital importance to the engineer. On three tests of pieces taken from the same cast iron bar, for instance, the variations in recovery were as great as 50 per cent.

C. Price-Green, of the Canadian National Railways, and B. F. Haanel, of the Canada Department of Mines, both told of the unlimited mineral resources and chances for development that their country offered to chemical engineers and to manufacturers. Mr. Price-Green discussed the phenomenal development of the Canadian chemical industry during the war. In speaking of the paper industry, he said:

> To-day the United States is mainly dependent upon Canada for its supply of paper and paper-making material, and the demand is a heavy one, as you use one-half the world's annual production of white paper. Canada is supplying 55 per cent of this demand. In 1890, Canada only exported to the extent of $120; to-day there are $250,000,000 invested in pulp and paper, and our annual production is valued at $120,000,000, and our exports $100,000,000, of which you receive 8 per cent.

After describing the method of peat formation and its physical and chemical properties, Mr. Haanel described methods of preparation of peat fuel, and gave statistics as to its heat value and industrial application.

W. D. Richardson, of Swift & Company, discussed the "Corrosion of Iron and Steel as Affecting the Industries," A. Hough and W. Savage spoke on the "Nitration of Hydrocarbons," and C. R. Bellamy pointed out some of the technical details in the operation of a modern by-product coke oven plant.

CERAMIC SYMPOSIUM

The Ceramic Symposium took the form of a meeting of the American Ceramic Society at which Chairman R. H. Minton read an abstracted committee report on "The Significance Attached to the Term Ceramics in Ancient and Modern Usage."

Charles F. Binns, in an address on "Ceramics and the People," pointed out the part the ceramic industries are playing in modern civilization, listing among their products cement, windows, drains, bricks, tile, wall tile, bathroom fixtures, sanitary fittings, electric light bulbs, glass screens for indirect lighting, sinks, and laundry trays.

ORIGINAL PAPERS

THE DETERMINATION OF CARBON MONOXIDE IN AIR CONTAMINATED WITH MOTOR EXHAUST GAS[1]

By M. C. Teague

TUNNEL GAS INVESTIGATIONS, U. S. BUREAU OF MINES, PITTSBURGH, PA.

Received August 12, 1920

In connection with the joint investigation of the Bureau of Mines and the New York-New Jersey State Bridge and Tunnel Commission with reference to the physiological effects of motor exhaust gas, it was of first importance to find a method for determining carbon monoxide in low concentrations and in the presence of other oxidizable gases.

The analytical determination of this gas in the concentrations here encountered (0.01 to 0.10 per cent) offers a much more difficult problem than the usual determination. The Orsat method, using ammoniacal cuprous chloride solution as the solvent for carbon monoxide, does not remove the last traces of the gas; 0.2 or more may not be absorbed.[2] The Haldane analyzer as modified by Burrell and Seibert,[3] when operated by an expert, does not exceed a precision of 0.01 per cent. The Haldane blood method,[4] although applicable to small concentrations, is subject to many variations, which do not always give concordant results.

The method which offered the greatest possibilities for the present work was that of iodine pentoxide, which consists in oxidizing the gas with iodine pentoxide and determining the amount either of carbon dioxide formed or of iodine liberated.

Considerable study of this method has been made since its first use in 1888.[5] A portable apparatus described by Graham[6] makes use of bromine in potassium bromide solution to remove any unsaturated hydrocarbons, and dries the gas with calcium chloride and phosphorus pentoxide before it enters the iodine pentoxide tube, which is held at temperatures between 90° and 150° C., there being no observed difference in results over this range, except in the presence of relatively large amounts of hydrogen. Under carefully controlled conditions, an accuracy to within 0.005 per cent carbon monoxide is claimed.

Lt. Col. A. B. Lamb[7] and his coworkers made use of the iodine pentoxide method in connection with their work on carbon monoxide absorbents for gas masks. At that time there was developed by A. T. Larson and E. C. White[1] a 6-unit multiple apparatus. This was designed for use with carbon monoxide-air mixtures only, although they experimented and found an interference by hydrogen. The purifying train included a tower of sodium hydroxide solution, another containing hot concentrated sulfuric acid, and finally a tube of dry alkali. The attempted accuracy was 0.01 per cent carbon monoxide.

There has been a difference of opinion among earlier investigators as to the advantages of determining the amount of carbon dioxide formed or that of the iodine liberated. Upon first inspection of the equation

$$I_2O_5 + 5CO \longrightarrow 5CO_2 + 2I$$

it would seem preferable to determine the carbon dioxide, since a relatively large amount of it is formed. At these very low concentrations, however, the complete absorption of carbon dioxide is an exceedingly difficult operation. For most types of absorption tubes there would be the inconvenience of using several such tubes or of passing the gas through the apparatus at a slower rate. Furthermore, it has been found undesirable to work with baryta solution much weaker than 0.02 *N*, whereas in determining the iodine liberated by the reaction 0.001 *N* sodium thiosulfate can be used, a difference which offsets the advantage of the greater amount of carbon dioxide formed.

APPARATUS—TYPE I

An apparatus practically the same as that of Larson and White was constructed with the view of adapting it for carbon monoxide determinations in dilute exhaust gases.

The iodine pentoxide tubes were made of about three-quarter inch pyrex tubing, with the U about 10 in. long. They were filled with alternate layers of glass wool and iodine pentoxide (each tube containing 30 to 40 g. of the latter). The arm on the exit side of the U-tube was somewhat longer than the other and tapered to make an interlock glass joint with the guard tube. A similar joint was made with the absorption bulb, thus removing the possibility of error due to rubber connections.

PREPARATION OF PENTOXIDE

After the apparatus was assembled it was necessary that the iodine pentoxide be conditioned before making any determinations. This was accomplished by raising the temperature to 220° to 230° C. for several hours, while air was drawn through. (Iodic acid begins to decompose at 170° C. to form water and iodine pentoxide.) With the water, considerable iodine was at first driven off. Two varieties of iodine pentoxide were tried: one, the ordinary commercial variety, prepared by the oxidation of iodine with fuming nitric acid, required about 25 hrs. heating; while the other variety, prepared by the chloric acid method,[2] required only about 15 hrs. heating. The tubes containing the latter variety gave lower blanks and seemed more active and therefore less sensitive to temperature changes than did the other tubes.

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[1] Published by permission of the Director of the Bureau of Mines and the Chief Engineer of the New York-New Jersey State Bridge and Tunnel Commission.

[2] G. A. Burrell and F. M. Seibert, "The Sampling and Examination of Mine Gases and Natural Gas," Bureau of Mines, *Bulletin* **42**, 48

[3] *Loc. cit.*, p. 17.

[4] Forthcoming Bureau of Mines Bulletin on "Physiological Effects of Motor Exhaust Gases."

[5] C. de la Harfe and F. Reverdin, *Chem. Ztg.*, **12** (1888), 1726; Maurice Nicloux, *Compt. rend.*, **126** (1898), 746; Armand Gautier, *Ibid.*, **126** (1898), 1299; **128** (1899), 487; L. R. Kinuicutt and G. R. Sanford, *J. Am. Chem. Soc.*, **22** (1900), 14; E. H. Weiskoff, *J. Chem. Met. Soc. S. Africa*, **9** (1909), 258; G. A. Burrell and F. M. Seibert, Bureau of Mines, *Bulletin* **42** (1913), 60.

[6] J. Ivon Graham, *J. Soc. Chem. Ind.*, **38** (1919), 10.

[7] In charge of the Defense Research Section, C. W. S., U. S. A.

[1] Appreciation is here expressed for the use of unpublished data relative to Larson and White's iodine pentoxide apparatus.

[2] This method will be described later by A. B. Lamb and W. C. Bray.

In making the determinations, the iodine pentoxide tube was usually maintained at a temperature of 150° C. One-liter samples were drawn through the apparatus and then displaced with outside air. The rate of flow was about 1 liter in 15 min. The liberated iodine was absorbed in one Bowen's absorption tube containing a 10 per cent potassium iodide solution, and titrated with sodium thiosulfate (0.002387 *N*) (1 cc. thio ≈ 0.15 cc. carbon monoxide at 25° C. and 760 mm. pressure, or 1.5 parts in 10,000 for a 1-liter sample).

EXPERIMENTS UPON CARBON MONOXIDE-AIR MIXTURES

The determinations made on carbon monoxide-air mixtures are summarized in Tables I and II. It is apparent that the temperature of the iodine pentoxide is not a sensitive factor when working with carbon monoxide-air mixtures. Table II shows the increased precision obtained by sweeping out the train more thoroughly.

TABLE I—EFFECT OF I_2O_5 TEMPERATURE

	Parts CO in 10,000		
	100° C.	150° C.	175° C.
	6.0	6.1	5.7
	5.6	5.7	5.7
	5.4	5.7	5.5
	5.8	5.9	5.7
	5.8	6.0	5.7
	6.2	6.2	6.1
MEAN,	5.8	5.9	5.7

TABLE II—VARIATIONS OF PRECISION WITH TIME OF SWEEPING THE TRAIN

Series No.	Procedure	No. of Determinations	Parts CO (Mean Value)	Maximum Variation from Mean (Parts CO)
1	Total time, 30 min. (15 min. for sample, and 15 min. for sweeping the train)	6	8.8	±0.4
2	Total time, 45 min. (15 min. for sample, and 30 min for sweeping the train)	6	4.1	±0.2
3	Total time, 60 min. (15 min. for sample, and 45 min. for sweeping the train)	6	4.9	±0.2
4	Total time, 60 min. (30 min. for the (1 liter) sample, and 30 min. (2 liter) for sweeping the train)	6	5.5	±0.3
5	Total time, 75 min. (15 min. for sample, and 60 min. for sweeping the train)	6	4.0	±0.1

EXPERIMENTS UPON EXHAUST GAS

Attention was next turned to the use of exhaust gases. Analysis showed the following constituents: carbon dioxide, carbon monoxide, oxygen, hydrogen, methane and perhaps other low saturated hydrocarbons, traces of unsaturated hydrocarbons, and some unburned gasoline.[1] Obviously, there were also water and varying amounts of oil-smoke particles.

The carbon dioxide was sufficiently removed by the sodium hydroxide. The concentrated sulfuric acid was heated to 160° C. that it might absorb any traces of unsaturated hydrocarbons, in addition to drying the gas.[2]

As noted above, several investigators had found hydrogen to be partly oxidized by the hot iodine pentoxide. In each case, however, the amount of hydrogen was relatively large, while in exhaust gases the hydrogen content varies up to about one-half that of carbon monoxide. The effect of such low concentrations had therefore to be determined.

While methane and ethane do not interfere with the iodine pentoxide reaction, Graham observed that normal pentane when present in large concentrations was slightly affected at the temperatures used (90° to 150° C.). If that was true, it was to be expected that gasoline (hexane and heptane) would undergo oxidation even more readily.

There were, therefore, three possible sources of difficulty in applying this apparatus to the determination of carbon monoxide in these mixtures, namely, the presence of hydrogen, smoke particles, and gasoline vapor.

The following determinations were made to compare the iodine pentoxide method with the Orsat and similar methods.

TABLE III—COMPARISON OF METHODS

Expt. No.	Method of Determining CO Concentration	CO Concentration (Calculated)	CO Found by I_2O_5 Method	I_2O_5 Value / (Calc. Value)
1	CO from formic acid (not analyzed)	In gassing chamber 1.98 parts	1.82	0.92
2	95 per cent CO, Henderson analyzer	In gassing chamber 3.9	3.86	1.00
3	Exhaust gas, Orsat method 6.7 per cent CO	In gassing chamber 3.0	3.90	1.30
4	Exhaust gas, Orsat method 6.5 per cent CO	In gassing chamber, approximately 2.8	3.50	1.25
5	Exhaust gas, Orsat method 8.4 per cent CO	In gassing chamber 1.0	1.34	1.34
6	Exhaust gas, Orsat method	In gassing chamber 13.5	17.8	1.32
7	Exhaust gas, Orsat method 6.3 per cent CO	Orsat buret to sampling tube, then diluted to 1 liter 10.29	13.77	1.34
8	Exhaust gas, 6.3 per cent CO	Orsat buret to sampling tube, then diluted to 1 liter 9.59	13.62	1.42

In Expts. 1 and 2 the pure carbon monoxide was measured in a graduated cylinder and displaced by water. In others, using the gassing chamber, the exhaust gas was displaced from a large graduated gasometer. In the last two experiments the exhaust gas was measured out of the Orsat buret directly into the sampling tube, and then diluted to about one liter.

The methods of diluting in the chamber were probably accurate to ± 10 per cent. Nevertheless, when exhaust gas was used, consistently higher results were obtained by the iodine pentoxide method. This increase varied with gas from different cars; on the car used for the above tests it was 30 to 40 per cent, while for another car it was 60 to 80 per cent. It was true that the cuprous chloride solution of the Orsat apparatus did not absorb the last traces of carbon monoxide, yet that unabsorbed could not account for the observed high results. It was evident that some one or more of the other constituents of the exhaust gas were also being oxidized by the iodine pentoxide.

EFFECT OF HYDROGEN—A mixture of carbon monoxide and air was prepared and analyzed. A known volume of hydrogen was then added to the remaining gas and the carbon monoxide again determined.

These experiments justify the conclusion that such quantities of hydrogen as occur in exhaust gases (about one-half the carbon monoxide concentration) are not sufficient at these low concentrations to influence the carbon monoxide determinations as obtained by the iodine pentoxide method. It was not until hydrogen was present in about twice the volume of carbon monoxide that any effect was observed in the above determinations, and even then the results were not conclusive.

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[1] Analyses made by G. W. Jones, Pittsburgh Station, Bureau of Mines.

[2] E. H. Weiskoff, *J. Chem. Met. Soc. S. Africa*, 9 (1909), 258.

EXPT. A: PARTS CO IN MIXTURE

	Without Hydrogen 150° C.	With Hydrogen = 0.5 Volume of CO 100° C.	With Hydrogen = 0.5 Volume of CO 150° C.	With Hydrogen = 1 Volume of CO 150° C.
	4.7	4.9	4.8	4.9
	4.8	4.9	4.9	...
MEAN,	4.8	4.9	4.9	4.9

EXPT. B: PARTS CO BY I_2O_5 METHOD (Temperature 150° C.)

	SERIES I Without Hydrogen	SERIES II 1.2 Parts CO and Approximately 2.2 Parts Hydrogen	SERIES III 1.2 Parts CO and Approximately 4.5 Parts Hydrogen
	1.3	1.5	1.9
	1.2	1.5	1.5
	1.3	1.6	1.5
	1.2	1.7	1.8
	1.1	1.6	1.9
	...	...	1.9
MEAN,	1.2	1.6	1.8

EFFECT OF SMOKE PARTICLES FROM THE OIL—Although a pad of glass wool was used in the sodium hydroxide tube just before the iodine pentoxide, it was possible for small smoke particles to pass through this and perhaps increase the iodine liberated. To determine whether or not this caused the observed high results from exhaust gas, a paper filter was inserted into the train. The filter was made by clamping two 11-cm. "quantitative filter papers" of good quality between two ground-edge funnels, permitting a filtering area of about 90 sq. cm.

The use of this filter made no difference in the determinations on exhaust gas, *i. e.*, the carbon monoxide determinations were the same as those when the filter was not used (60 to 80 per cent higher than the value calculated from the Orsat analysis).

EFFECT OF GASOLINE—Three determinations were made upon a mixture of carbon monoxide and air containing about 4 parts of carbon monoxide. Motor gasoline was placed in an Erlenmeyer flask, and the flask stoppered. After standing for several hours, a small portion of the flask atmosphere (equal to about 1 part gasoline in 10,000) was withdrawn by a Luer syringe and inserted into the above carbon monoxide-air mixture. The carbon monoxide equivalent in two samples of this mixture was determined on the same apparatus as used above.

PARTS CO OR EQUIVALENT

EXPT No.	Air + CO Mixtures	Air + CO + Gasoline Mixtures
1	4.1	7.0
2	4.3	7.2
3	4.0	...
MEAN,	4.1	7.1

It is evident from the above experiments that whereas the concentrations of hydrogen and smoke particles encountered in exhaust gases do not interfere in the I_2O_5 method of determining carbon monoxide, the unburned gasoline vapor does interfere to a considerable extent.

Several absorbents were tried for the removal of the gasoline vapor without affecting the carbon monoxide concentration.

(1) Cold concentrated sulfuric acid inserted in the train before the heated acid had no effect upon the results.

(2) Dry, activated coconut charcoal was known to be a good absorbent for gasoline vapor and at the same time useless for absorbing carbon monoxide. A tube of this absorbent was, therefore, inserted before the I_2O_5 tube in the place of the solid sodium hydroxide. With this arrangement the high results on exhaust gas were reduced to very nearly the calculated value. When determinations were made upon carbon monoxide-air mixtures, however, the carbon monoxide was appreciably absorbed by the charcoal.

(3) Many heavy mineral oils are also good absorbents of gasoline vapor at higher concentrations. A bead tower containing such an oil (Albolene) was therefore inserted in the train in front of the sulfuric acid tower. It was found that the vapor pressure of this oil was sufficiently high to cause an undesirable and somewhat variable blank due to its reaction with the I_2O_5. This was true at both room and freezing temperatures, and therefore prevented its use, even though it completely removed the gasoline vapor from exhaust gases.

(4) Shaved paraffin had no effect upon the results with exhaust gas or carbon monoxide-air mixtures. The average of three determinations on exhaust gas using the usual train showed an increase of 74 per cent over the calculated carbon monoxide value, whereas with the paraffin in the train an average of the same number of determinations showed an increase of 70 per cent. On the two procedures with carbon monoxide-air mixtures, the determinations checked.

(5) It was thought possible that by chilling the dried entering gases to —80° C., the gasoline would be condensed to droplets capable of being filtered out. The gas was led through a small U-tube containing glass wool and about which was packed carbon dioxide snow. With the failure of this to give the desired result, the tube containing the glass wool was replaced by one containing an alundum cylinder (Norton, medium porosity). The chilled gas was thus drawn through this porous cup. The results on exhaust gas were still unaffected.

(6) The next lower convenient temperature was that of liquid air. A similar U-tube containing glass wool was employed. While liquid gasoline cooled to this temperature (—190° C.) becomes a glass-like solid, it was realized that its vapor at such exceedingly low partial pressures might still prove difficult to completely remove.

A twenty-liter carbon monoxide-air mixture was prepared; three samples were withdrawn; and air containing gasoline vapor was injected into the remainder, and six samples taken. The carbon monoxide values of three of the latter samples were determined on the apparatus previously used (Type I) and three on the train with the liquid-air cooled tube.

	CO + Air Mixtures Old Apparatus Parts CO	CO + Gasoline + Air Old Apparatus Parts CO Equivalent	CO + Gasoline + Air "Liquid Air Tube" in Train Parts CO Equivalent
	8.3	48.0	7.8
	8.0	46.7	7.6
	7.5	46.0	7.8
MEAN,	7.9	46.9	7.7

Thus, at this temperature, the gasoline vapor was completely removed even under greatly exaggerated conditions. The liquid air temperature also condensed the water, carbon dioxide, and probably all of the unsaturated hydrocarbons.

APPARATUS—TYPE II

All of the members of the former purifying train were therefore removed, leaving only the liquid-air cooled tube (Type II apparatus, see Fig. 1). Repeated determinations showed the same results.

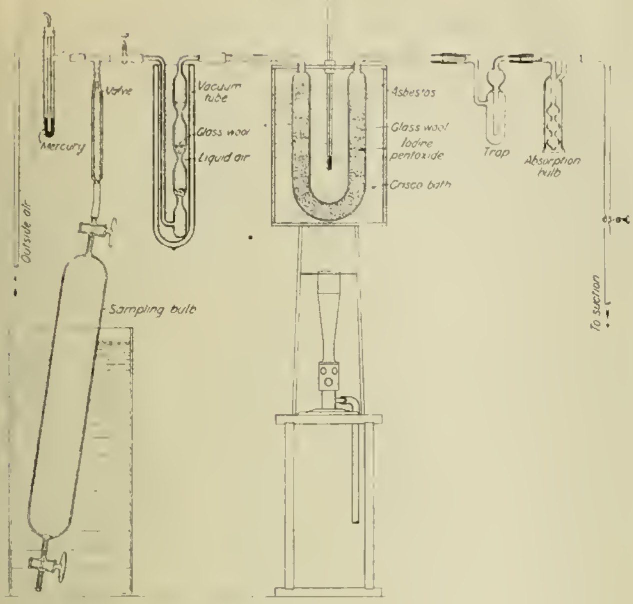


FIG. 1

CARBON MONOXIDE-AIR MIXTURES

	Type I Apparatus Parts CO	Type II Apparatus Parts CO
	5.8	5.2
	5.9	5.7
	5.7	5.4
	4.9	5.0
MEAN,	5.6	5.3
	16.1	16.4
	16.2	16.3
MEAN,	16.2	16.4

In the following tables are found the results of numerous determinations on exhaust gases. From the results it is noted that at liquid air temperature all of the gases in dilute exhaust gas which interfere with the accurate carbon monoxide determination by the I_2O_5 method are removed.

EXHAUST GAS CONTAINING 3.8 PER CENT CO FROM MACHINE IN APPARENTLY GOOD CONDITION

Measured from Gas Buret Cc. CO Taken	—Type I Apparatus—		—Type II Apparatus—	
	Cc. CO Found	Per cent of CO Calculated	Cc. CO Found	Per cent of CO Calculated
1.16	..	...	1.12	97
1.05	..	...	1.08	103
0.80	0.87	111	..	...

EXHAUST GAS CONTAINING 4.0 PER CENT CO FROM ARMY TRUCK WITH ONE CYLINDER NOT FUNCTIONING

Measured from Gas Buret Cc. CO Taken	—Type I Apparatus—		—Type II Apparatus—	
	Cc. CO Found	Per cent of CO Calculated	Cc. CO Found	Per cent of CO Calculated
0.99	..	...	1.06	107
1.04	1.73	166	..	...
0.63	..	...	0.59	94
0.57	0.94	170	..	...
0.65	..	...	0.64	99
0.64	1.03	161	..	...
	MEAN,	166		100

EXHAUST GAS CONTAINING 9.6 PER CENT CO FROM ARMY TRUCK (ENGINE RACING)

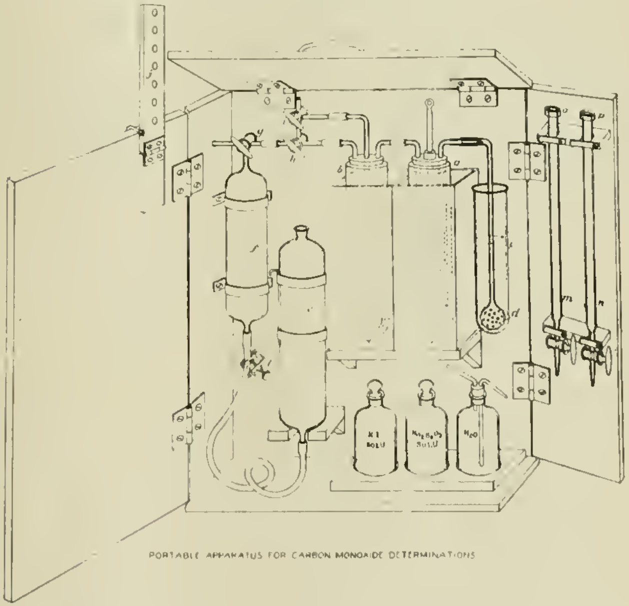
Measured from Gas Buret Cc. CO Taken	—Type II Apparatus—	
	Cc. CO Found	Per cent of CO Calculated
0.78	0.79	101
1.03	1.04	101
1.16	1.19	103
	MEAN,	102

In Type II the Dewar vacuum tube has replaced four members of the Type I purifying train. This simplified apparatus will probably reduce the time per determination by 50 per cent, owing to the shorter time necessary to clear the train completely. The elimination of liquid seals also facilitates the manipulation. Blank determinations on Type II were constantly at zero. About 300 cc. of liquid air were used per train per day.

PORTABLE APPARATUS

A convenient method for accurately determining carbon monoxide in such mixtures as dilute exhaust gas having been developed, it was further modified into a portable apparatus for use in exploring vehicular tunnels, garages, and other enclosed places where it is desired to determine low carbon monoxide concentrations, in the absence of relatively large amounts of hydrogen.

The apparatus is shown in Fig. 2. The gas sample, which has been reduced to 500 cc., is drawn into tube *f* by use of the leveling bulb *e*, and through 3-way cock *g*. *b* and *a* are stoppered vacuum cylinders (8 to 10 in. tall) containing U-tubes immersed in liquid air and hot Crisco oil, respectively. In the cold U-tube are condensed the water vapor, carbon dioxide, gasoline vapor, and traces of other saturated and unsaturated hydrocarbons. The hydrogen, methane, and carbon monoxide pass on into the iodine pentoxide U-tube immersed in the oil bath *a* heated to 100° to 175° C. Only the carbon monoxide is oxidized by the iodine pentoxide (the concentration of hydrogen in dilute exhaust gas being too low to be affected). The liberated iodine is absorbed in potassium iodide solution in test tube *c*, using the bubbler as shown in the sketch, and titrated with sodium thiosulfate from buret *n*. Buret *m* is used for the starch solution.



PORTABLE APPARATUS FOR CARBON MONOXIDE DETERMINATIONS

FIG. 2

By filling the Dewar tubes before starting to work, they will be found quite sufficient for a day's work, which will be much too long for the operator to remain in most atmospheres containing carbon monoxide.

In making a determination, a sample is drawn into *f* by means of *e* (filled with water), and slowly passed through the apparatus. The rate of flow is regulated by placing tube *e* on rack *j* and adjusting the pinchcock *l*. From 6 to 7 min. is the best rate for a 500-cc.

sample. During this procedure, stopcock *i* is turned to permit the evaporating liquid air to escape into the atmosphere. Since the apparatus must be cleared with fresh air and the determination is being made in the gas to be tested, stopcocks *i* and *h* are now turned to place the liquid air chamber in communication with *f* and the tube thus filled with "pure air" for sweeping the train.

The apparatus is contained in a cabinet 24 in. × 20 in. × 7 in.

A determination should take about 15 min. and should be accurate to from 0.003 to 0.005 per cent carbon monoxide (0.3 to 0.5 part in 10,000).

SUMMARY

The iodine pentoxide method for determining low concentrations of carbon monoxide has been investigated with reference to its use with dilute motor exhaust gas. The type of apparatus heretofore used was found to give appreciably high results owing to the presence of small amounts of unburned gasoline. A new iodine pentoxide apparatus (Type II) has therefore been developed. All of the interfering gases are first removed at the temperature of liquid air. This method has been found quite satisfactory for determining carbon monoxide in small quantities in the presence of gasoline vapor.

A portable iodine pentoxide apparatus has been designed which should permit a determination to be made in 15 min. with an accuracy of from 0.003 to 0.005 per cent carbon monoxide (0.3 to 0.5 part in 10,000).

ACKNOWLEDGMENT

Appreciation is expressed to Dr. A. C. Fieldner, supervising chemist in charge of tunnel gases investigation, and Dr. Yandell Henderson, in charge of physiological investigations, for valuable suggestions and advice, and to Mr. W. B. Fulton for making many of the determinations herein reported.

THE USE OF CATALYSTS IN THE SULFONATION OF AROMATIC COMPOUNDS

By Joseph A. Ambler and William J. Cotton

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Received May 12, 1920

During the course of experimentation on the vapor-phase sulfonation of compounds, it was found that by using the continuous method of Ambler and Gibbs,[1] with a given set-up of apparatus and given temperature range, the amount of material sulfonated per minute was practically constant; that is, the apparatus had a certain "capacity" for sulfonation, since so long as the baffles in the apparatus were not disturbed, the free space for vapors and the absorbing or sulfonating surface were constant. The method, therefore, provided a good means of studying the effect of various substances introduced with the reacting materials, and of ascertaining which were catalyzers of the sulfonation reaction. This work is intended as introductory to a much more complete study of sulfonation catalysts. Inasmuch as the study will be unavoidably delayed for some time, it seems best to publish the work thus far accomplished, although it is incomplete.

Various workers have reported that the sulfonation of aromatic compounds may be accelerated by adding different catalysts. The addition of sodium sulfate[1] or various acid sodium sulfates[2] has long been common practice, and a similar use of potassium sulfate[3] has also been reported. It is also well known that various sulfonic acids can easily be further sulfonated in the form of their sodium or potassium salts; whereas, if the free acid is used, the introduction of more sulfonic acid groups becomes extremely difficult, as, for example, in the production of benzene-1,3,5-trisulfonic acid[4] from the salts of benzene disulfonic acid. In all of these cases, the large amount of the alkali salts used makes it almost impossible to decide whether the action is catalytic, or caused by the greatly increased boiling point of the sulfuric acid-alkali sulfate mixture used.

Other substances recommended as accelerating catalysts are vanadium[5] in the sulfonation of anthraquinone, and iodine[6] in the sulfonation of benzene. Compounds of mercury, aluminium, iron, lead, arsenic, bismuth, cadmium, and manganese[7] have also been studied from the standpoint of their effect upon the position in the molecule taken by the entering sulfonic acid group.

EXPERIMENTAL DETAILS

In the present work some of the compounds mentioned above have been studied to ascertain whether they exert any accelerating (catalytic) effect on the sulfonation of benzene, and all so far examined have shown some catalytic action. These substances are copper sulfate, mercuric sulfate, vanadium pentoxide, sodium sulfate, chromic acid, potassium sulfate, lithium sulfate, and mixtures of sodium sulfate and vanadium pentoxide. In every case the substance was dissolved in 70 per cent sulfuric acid, thus insuring a constant concentration of the catalyst in the reaction tower. The concentration of catalyst is expressed as the percentage of the characteristic element, although in making the solutions the above-mentioned compounds were actually added to the sulfuric acid. For example, 0.1 per cent copper means that the amount of copper sulfate used was chemically equivalent to that weight of copper which was 0.1 per cent of the weight of the sulfuric acid.

In each case the experiment was carried on for from an hour to an hour and a half, after which time the products of the reaction were discarded, at the same time "cutting in" with weighed quantities of acid and benzene. The experiment was considered as starting from this point in order to be sure that the reaction had become thoroughly established and that everything about the apparatus was in a state of equilibrium which could be maintained until the end of the experiment; and to obviate the large error inherent in the apparatus, due to the fact that it took some time for the benzene vapors to displace all the air in the apparatus, and for the sulfuric acid to wet all the surfaces of the baffles and the walls of the tower, during which time the apparatus did not operate at its maximum capacity.

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[1] U. S. Patents 1,292,950; 1,300,227; 1,300,228. A description of this process will be published in subsequent papers.

[1] Girard, *Bull. soc. chim.*, **25** (1876), 333; Mühlhäuser, *Dingler's polytech. J.*, **263** (1887), 154.

[2] Lambert, D. R. P. 113,784 (1899); Kendall, U. S. Patent 1,217,462 (1917).

[3] Jackson and Wing, *Am. Chem. J.*, **9** (1887), 325.

[4] Jackson and Wing, *Loc. cit.*; Bebrend and Murtelsmann, *Ann.*, **378** (1911), 352.

[5] Thümmber, D. R. P. 214,156 (1909).

[6] Hinemann, Brit. Patent 12,260 (1915).

[7] Iljinsky, *Ber.*, **36** (1903), 4194; Schmidt, *Ibid.*, **37** (1904), 66; Dünschmann, *Ibid.*, **37** (1904), 331; Holdermann, *Ibid.*, **39** (1906), 1250; Dimroth and Schmaedel, *Ibid.*, **40** (1907), 2411; Behrend and Mertelsmann, *Loc. cit.*; Mohrmann, *Ann.*, **410** (1915), 373.

TABLE I

Catalyst	Concentration Per cent	Mean Temp. ° C.	Duration of Expt. Min.	Wt. Sulfonic Acids Grams	Wt. Benzene Sulfonated per Min. Grams
...	...	243	580	734	0.63
Cu	0.1	251	185	301	0.80
Hg	0.1	243	232	386	0.82
V	0.1	249	249	356	0.71
Na(I)	0.1	252	291	649	1.10
Cr	0.1	249	202	278	0.67
K	0.17	257	292	479	0.82
Li	0.094	246	283	405	0.61
Na(II)	0.5	255	300	492	0.83
Na(III)	0.1	259	355	601	0.84
Na V	0.1 0.05	242	274	626	1.13
V Na	0.223 0.025	249	232	592	1.26

Tables I and II give the critical data so far as the catalysts are concerned. The "weight of sulfonic acids" in Table I was found as follows: Total acidity, expressed in terms of sulfuric acid, was determined by titration with standard alkali, using phenolphthalein or thymolsulfophthalein for indicator. Actual sulfuric acid was determined with barium chloride as usual. The difference of these two determinations represented sulfuric acid equivalent to the sulfonic acid present. The latter was temporarily assumed to be benzene monosulfonic acid, and its amount calculated according to the ratio $H_2SO_4 : 2HSO_3.C_6H_5$. From this value it was a simple matter to calculate the amount of benzene sulfonated per minute.

TABLE II

Catalyst	Concentration, Per cent	Mean Temp., ° C.	Duration of Expt., Min.	Wt. Sulfonic Acids Grams (Corr.)	Wt. Disulfonic Acid Grams	Wt. Benzene Sulfonated per Min. Grams	Wt. Disulfonic Acid Produced per Min. Grams
..	...	243	580	705	147	0.56	0.25
Cu	0.1	251	185	294	28	0.76	0.15
Hg	0.1	243	232	377	36	0.78	0.16
V	0.1	249	249	355	6	0.66	0.03
Cr	0.1	249	202	274	13	0.66	0.06
Li	0.094	246	283	380	95	0.61	0.34
Na(II)	0.5	255	300	463	111	0.70	0.37
Na(III)	0.1	259	356	574	101	0.75	0.29
Na V	0.1 0.05	242	274	595	121	1.00	0.44
V Na	0.223 0.025	249	232	569	88	1.15	0.39

These figures, however, were subject to error, inasmuch as some benzene disulfonic acid was always formed. Table II contains corrected values, based on the following calculation: The amount of disulfonic acid was determined by analysis of the barium salt of the sulfonic acids, making necessary corrections for the catalyst itself when it was found in the barium salt. The weight of sulfonic acids was then corrected and, by using the two ratios $C_6H_6 : C_6H_5SO_3H$ and $C_6H_6 : C_6H_4(SO_3H)_2$, the amount of benzene actually sulfonated per minute was calculated.

It should be noted here that two experiments given in Table I do not appear in the second, *viz.*, Na(I) and K. Through an unfortunate oversight the amount of benzene disulfonic acid was not correctly determined, because no determination of the amount of catalyst contained in the barium salt was made.

The experiment with no catalyst is typical of many in which the amount of benzene sulfonated per minute was always approximately 0.5 g. This figure represents the normal capacity of the apparatus.

DISCUSSION OF RESULTS

A study of Table I shows that all the substances used increased the amount of benzene sulfonated per minute, and that these catalysts are divided into two general groups, *viz.*, those which have a slight catalytic action, copper, mercury, vanadium, chromium, potassium, lithium, and two of the experiments with sodium; and those which have a marked catalytic action, the first experiment with sodium, and the two experiments using both sodium and vanadium. The more marked effect in the first experiment with sodium was caused by a small amount of vanadium, which had been used in the experiment just preceding it, and which had not been completely removed from the tower.

The most active catalyzer is obviously a mixture of sodium and vanadium in any reasonable proportion. The results also clearly show that the sodium and potassium sulfates in sulfonation mixtures have a distinct catalytic effect, and that the advantages gained by their use are not entirely due to the increased boiling point of the sulfuric acid.

Another interesting fact brought out is the effect of the catalyst on the amount of disulfonic acid formed per minute. This subject is to be investigated further. Apparently the members of the first group of the periodic system, represented here by sodium and lithium, accelerate the formation of disulfonic acid in this type of sulfonation, while the mixture of vanadium pentoxide with sodium sulfate is still more effective. The other catalysts apparently inhibit the formation of disulfonic acid.

PHTHALIC ANHYDRIDE. IV—THE VAPOR PRESSURE OF PHTHALIC ANHYDRIDE

By K. P. Monroe

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Received June 1, 1920

The investigation of the vapor-pressure curve of phthalic anhydride was initiated to assist in the solution of certain problems arising in the air-oxidation process recently developed by Gibbs[1] and his coworkers. Although the results were obtained in a preliminary series of measurements, and are not of the order of accuracy which it was hoped to obtain by repetition with a more refined mercury gage, they are presented, since it appears unlikely that the author will resume the investigation.

Phthalic anhydride, purified by a method previously described,[2] was placed in a static isoteniscope of the type designed by Smith and Menzies,[1] which was clamped vertically in a paraffin bath and connected, after the fashion described by these authors, to a vacuum pump, mercury gage, and a large iron cylinder which served as low pressure reservoir. The bath was a large unsilvered Dewar flask supported by felt-covered rings and filled nearly to the brim with paraffin which was stirred violently by a turbine. Constant temperature was maintained by an electrical heating device consisting of a nichrome coil wound on a glass tube snugly fitted into an outer glass tube sealed at one end. By means of a lamp-board connected to the 110-volt lighting circuit the current passing through the coil was accurately adjusted to maintain the temperature, which was measured by a calibrated Reichsanstalt thermometer completely immersed in the bath. After constant temperature (within ±0.05°) had been maintained for 15 min., the anhydride contained in the isoteniscope was boiled by maintaining a pressure somewhat less than the vapor tension. Air was then admitted cautiously in the reservoir until the levels of liquid anhydride became equal, and the gage was read. The boiling-out process was then repeated and another reading taken. This procedure was continued until the gage readings became constant and all dissolved gases had been expelled. The gage readings were corrected to 0° C.

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[1] See the previous articles of this series: "Phthalic Anhydride," I, by H D Gibbs, THIS JOURNAL, **11** (1919), 1031, "Phthalic Anhydride," II and III, by K P Monroe, *Ibid.*, **11** (1919), 1116 and 1119.

[2] Part II, *Loc. cit.*

TABLE I—VAPOR PRESSURE OF PHTHALIC ANHYDRIDE

p (Mm. of Hg)	t (° C.)
130.5	212.0
172.1	222.0
241.2	234.6
287.1	241.5
369.4	252.4
759.3	284.6[1]

[1] Compare 276°, Lossen *Ann*, **144** (1867), 76; 284.5°, Graeke, *Ber.*, **17** (1884), 1176.

The following interpolation formula was found to fit these data:

$$\log_{10} p = 7.94234 - \frac{2823.5}{T} \qquad (1)$$

when p = vapor pressure in millimeters of mercury, and T = absolute temperature.

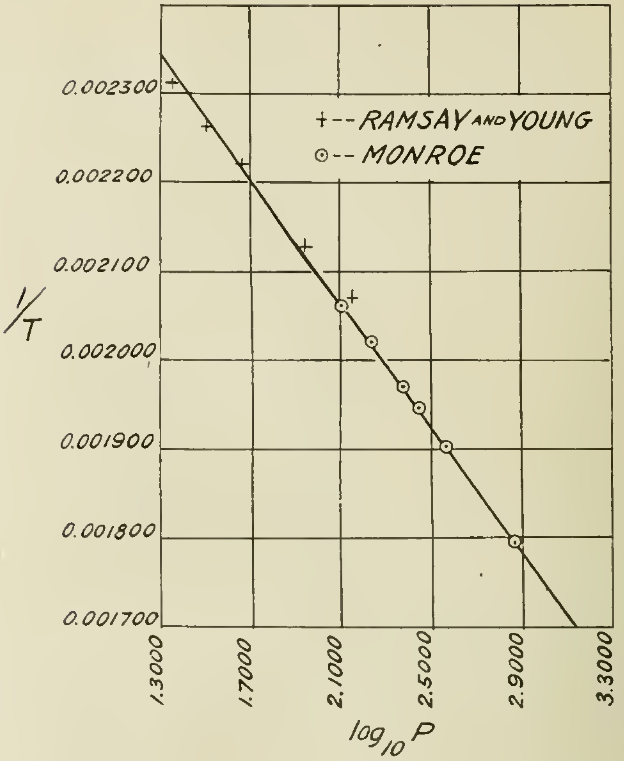
TABLE II—COMPARISON OF OBSERVED AND CALCULATED TEMPERATURES

p	T (Observed)	T (Calculated)
130.5	485.0	484.6
172.1	495.0	494.8
241.2	507.6	507.8
287.1	514.5	514.8
369.4	525.4	525.3
759.3	557.6	557.8

Since Ramsay and Young[2] have carried out a series of measurements of the vapor pressure of phthalic anhydride over a different temperature range than the one explored in this investigation, and with a different type of apparatus, it is of interest to compare the vapor tensions found by these investigators with the values calculated by Equation 1.

TABLE III—COMPARISON OF CALCULATED VAPOR PRESSURES WITH DATA OF RAMSAY AND YOUNG

t (° C.)	p (Observed)	p (Calculated by Equation 1)
159.5	22.8	26.0
168.6	32.2	35.3
177.1	46.9	46.7
196.9	87.3	85.8
210.1	142.0	125.3



The molar latent heat of vaporization of phthalic anhydride may also be calculated by Equation 1, for this equation is of the simple type obtained by integrating the Clausius-Clapeyron equation:[1]

$$\frac{dp}{dT} = \frac{L}{(V - v)T} \qquad (2)$$

where L = molar heat of vaporization, V = volume of mole of gaseous phase, v = volume of mole of liquid phase, T = absolute temperature, with the assumptions: (1) that the volume of a mole of liquid phase is negligible compared with that of a mole of gaseous phase; (2) that the gaseous phase obeys the perfect gas law; and (3) that the heat of vaporization does not vary with temperature.[2] Integrating and introducing Napierian logarithms:

$$\log_{10} p = C - \frac{0.4343\ L}{RT} \qquad (3)$$

when R = the gas constant, and C is a constant of integration.

Since

$$\frac{0.4343\ L}{R} = 2823.5 \qquad (4)$$

the molar heat of vaporization of phthalic anhydride is calculated to be 12,910 calories.

According to the criterion suggested recently by Hildebrand,[3] phthalic anhydride is shown by the data of this investigation to behave as a *normal* liquid, for the value 13.6 is obtained for the entropy of vaporization divided by R at the temperature (near 218°) at which the concentration of vapor is 0.00507 mole per liter. This value coincides with the average obtained from Hildebrand's table, based upon the vapor pressure curves of fifteen normal liquids.

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[1] *J. Am. Chem. Soc.*, **32** (1910), 1412, 1434, 1448

[2] *Trans. Roy. Soc. London*, **1886**, I, 102

[1] Washburn, "Principles of Physical Chemistry," McGraw-Hill Book Co., New York, **1915**, p. 123.

[2] None of these assumptions is, of course, strictly valid. The accompanying figure, however, reveals their justification by the experimental data over the somewhat limited temperature range, which is probably far below the unknown critical temperature of phthalic anhydride

[3] *J. Am. Chem. Soc.*, **37** (1915), 970

THE EFFECT OF CERTAIN ACCELERATORS UPON THE PROPERTIES OF VULCANIZED RUBBER—II[1]

By G. D. Kratz and A. H. Flower

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In a recent paper,[2] H. P. Stevens has given new figures, and from them made a number of deductions in regard to certain discrepancies between results obtained by the present authors[3] and earlier results obtained by him.[4] We do not entirely agree that these latest deductions will suffice for the complete coördination of his former results with ours. This view is confirmed by the repetition and amplification of our former experiments, including work with extra light instead of heavy calcined magnesia.

This work was carried out with a sample of the rubber previously employed and also with another rubber of similar physical appearance. Entirely different results were obtained with the two rubbers. In neither instance, however, was extra light magnesia found to develop greater activity than Accelerator A, and, in one case, it was markedly inferior to the latter. In both cases where Accelerator A was employed, the load required to effect a given extension led to erroneous conclusions, if used as a criterion of the rate of cure.

As these results were obtained with accelerators of definite composition and purity, the differences may be attributed to variations existing in the rubbers themselves, and most probably in the nature, amount, or condition of the extraneous materials present. As a considerable portion of this extraneous matter was extractable with acetone, an investigation was made of the relative effect of the two accelerators upon the two rubbers after extraction. Since the nature of the substances removed by the extraction[5] was not studied, no attempt can be made to correlate the effect of the extra light magnesia with any definite one of the extraneous substances originally present in the rubber. Certain facts, however, have been well enough established to deserve brief consideration.

It was noted by Spence[6] that the nitrogen in rubber was not entirely of protein origin, and that nitrogenous bodies of well-defined alkaloidal character could be detected in the acetone extract of Para rubber. This was subsequently confirmed by Spence and Kratz[7] for plantation crepe (Hevea), although a difference in the character of the protein material in the two rubbers was found. Further, certain of their results indicated that in plantation Hevea the non-protein nitrogenous substance was not easily extractable with acetone. Dekkar[1] also noted the presence of nitrogen in the acetone extract, and gave figures for nitrogen distribution in the extracted rubber and its acetone extract which closely confirmed those originally obtained by Spence. Prior to Dekkar's observations, Beadle and Stevens[2] noted that the rate of vulcanization of certain rubbers decreased if the rubbers were previously extracted with acetone. After vulcanization the physical properties of the acetone-extracted samples were so greatly impaired, due either to the loss of the resin or the physical effect of the solvent upon the rubber, that the decrease in the rate of cure was considered of secondary importance.

It would therefore appear that the removal of the acetone-soluble nitrogenous constituent is responsible for the decrease in the rate of cure of the rubbers, rather than either of the causes originally assigned by Beadle and Stevens.[3] This is also in accordance with the later results of Eaton, Grantham and Day,[4] and of Stevens,[5] wherein the accelerating substance of plantation Hevea rubber was found to be an organic base or mixture of bases, probably formed by the degradation of the protein portion of the nitrogenous material originally present in the rubber.[6]

The possibility that magnesia may hasten this degradation, with the formation of an accelerator similar to that produced by the biological decomposition of the proteins, has already been pointed out by Eaton[7] in commenting upon the patent of Esch.[8]

In view of the well-known action of many synthetic organic accelerators in the presence of certain mineral oxides, such as that obtained by Cranor[9] with zinc oxide, we are led to the conclusion that the effect of small amounts of magnesia in accelerating the vulcanization of rubber is of a secondary or contributory, rather than a primary nature, and consists largely in effecting a response from the natural accelerator in the rubber. This finds further confirmation in the observation of Stevens in his previous paper, wherein he pointed out that the accelerating effect of extra light magnesia decreases when a sulfur coefficient of

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[1] Presented at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

[2] *India Rubber J.*, **58** (1919), 527.

[3] *Chem. and Met. Eng.*, **20** (1919), 417.

[4] *J. Soc. Chem. Ind.*, **37** (1918), 156*t*.

[5] A qualitative determination showed the presence of nitrogen in the extracts of both rubbers.

[6] Herbert Wright, "*Hevea Bras.*, or Para Rubber," **1912**, p. 439. London.

[7] *Kolloid-Z.*, **14** (1914), 268.

[1] Comm. of the Neth. Govt. Inst. for Advising the Rubber Trade and Rubber Industry, Part II, p. 55.

[2] *Intern. Congr. Appl. Chem.*, **25** (1912), 581.

[3] In a previous paper [This Journal, **12** (1920), 317], we have mentioned that results obtained with certain synthetic organic substances indicate, in some cases, that the accelerator may be closely bound to the rubber. Should this also be found true in the case of the natural accelerator, the removal of this substance by extraction would markedly impair the physical properties of the sample after vulcanization, as well as slow down the rate of cure. (Compare with footnote, p. 974.)

[4] "Variability in Plantation Rubber," *J. Soc. Chem. Ind.*, **35** (1916), 715.

[5] *J. Soc. Chem. Ind.*, **36** (1917), 365.

[6] The protein portion of this nitrogenous material which is insoluble in acetone and benzene has been shown to act as an accelerator (Beadle and Stevens, *Kolloid-Z.*, **11** (1912), 61; **12** (1913), 46; **14** (1914), 91). It has the further advantage of being present in relatively large amount as compared with the acetone-soluble constituent. As it does not, however, respond to magnesia to the same extent as the latter substance, and, as certain results (not included in this paper) indicate that the extraction with acetone does not cause a marked degradation of this protein material into the soluble variety, we have not made reference to it.

[7] *Agr. Bull. Federated Malay States*, **5** (1915), 38.

[8] Ger. Patent 273,482 (Nov. 22, 1912)

[9] *India Rubber World*, **61** (1919), 137

2.0 to 2.5 has been attained. At this point, increased amounts of magnesia would have no effect, as they would be in excess of the amount required by the natural accelerator, which is present in the same definite and limited amount in all of the mixtures.[1]

The same would not be true for Accelerator A, which is regarded as a primary accelerator and is present in the various mixtures in increasing amounts up to 1 per cent of the rubber.

In conclusion, we wish to draw a distinction between the terms "effect of accelerators" and "action of accelerators." This paper deals primarily with the effect produced by certain accelerators upon the sulfur coefficient and the physical properties of the rubber after vulcanization. The action of these accelerators, *per se*, is another problem entirely. We are convinced, however, that in many instances both the action and effect of organic accelerators is dependent in great extent upon the presence of certain mineral substances in the mixture.

EXPERIMENTAL PART[2]

The experimental procedure was similar in all respects to that of our former experiments. Essentially it differs from that of Stevens only in the method of vulcanizing, and in the substitution of straight pieces for physical tests in place of the rings employed by him. The relative effects of vulcanization in steam and in a platen press are commented upon later.

Two samples of thin, pale, first latex crepe (Hevea) were used. Sample 408 was from the lot of rubber that was used in our former experiments, while Sample 444 was chosen from another lot of equally good appearance, which was found to have different chemical and physical characteristics when employed in factory mixtures.

A partial analysis of the two rubbers gave the following results. No great importance, however, is attached to the figures for total nitrogen.

	No. 408 Per cent	No 444 Per cent
Total Ash	0.26	0.29
Acetone Extract	2.62	2.99
Total Nitrogen	0.19	0.20

The extra light magnesia (sp. gr. 3.45) was the best grade obtainable. It lost 4.00 per cent on ignition, after which it contained 93.67 per cent MgO. Accelerator A was prepared by the condensation of an amine with formaldehyde and was C. P. grade.

The conditions of milling and making physical tests were identical with those previously employed, but, as comparisons were made after the method of Stevens, the physical properties of the different mixtures at break have been omitted.

Sulfur determinations were made by our method[3] in place of that of Rosenstein-Davies.[4] The coefficients represent the combined sulfur of vulcanization expressed as a percentage of the rubber in the mixture.

Throughout the work all cures were made in a platen press of the usual type. Stevens' samples were wrapped with cloth and vulcanized in steam.[1]

EXPT. I—This work consisted virtually of a repetition of the previous work, using the sample of rubber (No. 408) previously employed, but substituting extra light magnesia for the heavy calcined material used in our former experiments. The results are given in detail in Table I,[2] and the relation between sulfur coefficients and amount of accelerator is shown graphically in Fig. 1. The relation between the amount of accelerator and the load required to effect a given extension is also shown in Fig. 1. In both cases these results confirm previous ones, even to the shape of the curves themselves. As has already been stated, if accelerators (such as our Accelerator A) are present in the mixture even in small amount, it is evident that the load required to effect a given extension is not a measure of the physical properties of the mixture, nor is it a reliable criterion of the rate of cure of the vulcanized mixtures.

TABLE I—TESTS ON RUBBER NO. 408

Accelerator	Accelerator Per cent	Sulfur Coefficient		Load in Hectograms per Sq. Mm. to Effect Extension					
				1 to 7		1 to 8		1 to 9	
		Actual	Excess	Actual	Excess	Actual	Excess	Actual	Excess
Extra Light Magnesia	Control	0.580	...	0.34	....	0.42	....	0.50	....
	0.10	0.704	0.124	0.58	0.24	0.74	0.32	0.94	0.44
	0.25	0.916	0.336	1.03	0.69	1.37	0.95	1.98	1.48
	0.50	1.874	1.294	2.09	1.65	3.20	2.78	5.11	4.61
	0.75	2.553	1.973	3.03	2.69	4.84	4.42	8.17	7.65
	1.00	2.599	2.019	3.21	2.87	5.17	4.75	8.92	8.42
Accelerator A	Control	0.580	...	0.34	....	0.42	....	0.50	....
	0.10	1.356	0.776	0.88	0.54	1.10	0.68	1.61	1.11
	0.25	1.987	1.407	1.70	1.36	2.25	1.83	3.57	3.07
	0.50	2.925	2.345	2.14	1.80	2.77	2.35	4.23	3.73
	0.75	3.309	2.729	2.16	1.82	2.72	2.30	4.32	3.82
	1.00	3.603	3.023	2.30	1.96	2.98	2.56	4.81	4.31

EXPT. II—This consisted of a repetition of Expt. I upon Sample 444. The results are given in Table II, and the relation between sulfur coefficients and the amount of accelerator, and between the amount of accelerator and the load required to effect a given extension are shown in Fig. 1. On the basis of the sulfur coefficients, Accelerator A and extra light magnesia appear to be of almost equal activity; or, conversely, Sample 444 vulcanizes at the same rate with either accelerator. When judged by the load required to effect a given extension, however, extra light magnesia appears to be much the more active. As it is now almost generally conceded that sulfur coefficients

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[1] It is interesting to note that Dekkar's figures for the nitrogen in the acetone extract of Hevea crepe (when calculated on a protein basis) are very close to the amounts of the accelerators employed in these experiments.

[2] In collaboration with Bernard J. Shapiro.

[3] *India Rubber World*, **61** (1920), 356.

[4] *Chemist-Analyst*, **16** (1916), 4.

[1] Stevens in his first paper on this subject has mentioned the possibility of a difference in the rate of cure of accelerated mixtures when vulcanized in dry heat. We have found similar mixtures which contained magnesia to show increasingly large sulfur coefficients when vulcanized, respectively, in dry heat, platen press, and open steam. This was not found to be true, however, for mixtures which contained organic accelerators. With the latter, results obtained in a platen press were frequently higher than those obtained in open steam. Evidently many organic accelerators are partially soluble in, or volatile with steam and, consequently, results obtained with these substances in open steam are apt to be low. This point is of considerable importance, and accounts in large part for the difference in the results obtained by Stevens and ourselves. We have found that most uniform results are obtained with samples encased in molds and vulcanized in open steam.

[2] The results obtained and shown in this table are somewhat higher than those originally found, and which were given in Table I of our former paper. This discrepancy may be attributed to a change in the rubber itself, as the sample used in the present instance had aged for over one year in roll form in a partially broken-down condition before the experiment was repeated. Also, the method previously employed for the estimation of combined sulfur was found to give slightly low results for mixtures which contained but small amounts of mineral substances.

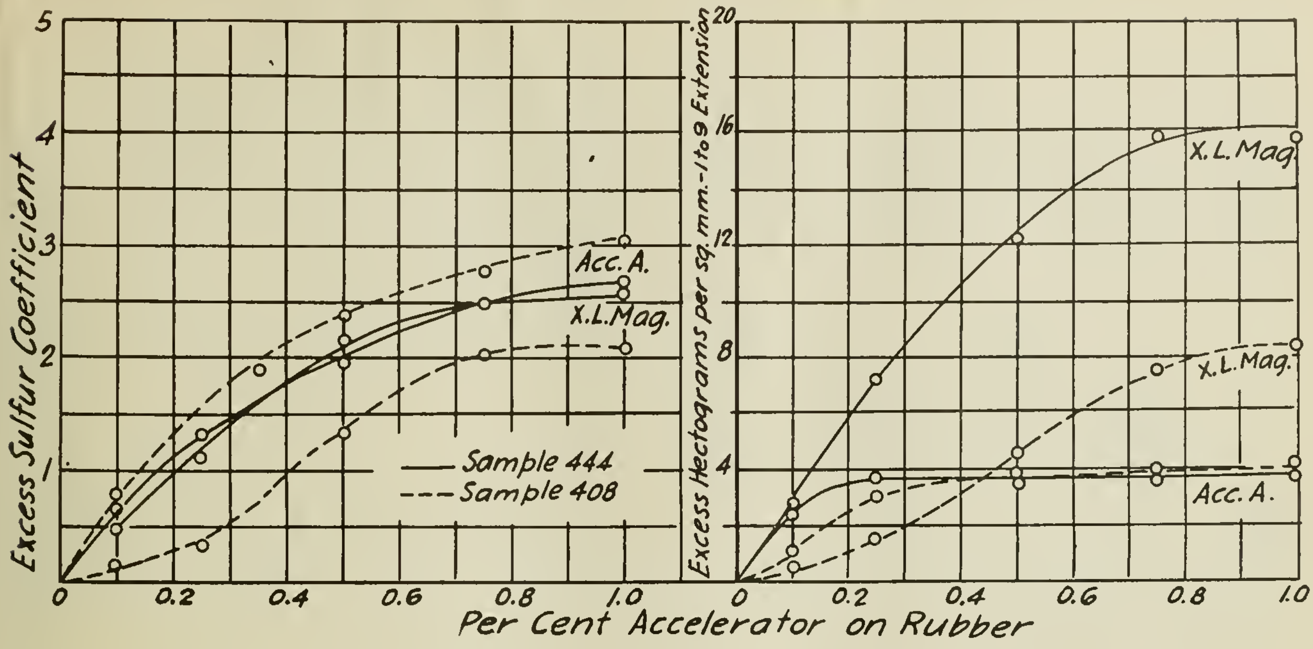

Fig. 1

afford the most reliable indication of the state of cure, the load required to effect a given extension is again seen to be unreliable as an indication of the rate of cure of accelerated mixtures. These results have strengthened our former opinion that, unless a complete series of stress-strain measurements are made, when the results of physical tests are taken as measure of the rate or state of cure of accelerated mixtures, such measurements must be made at or near the point of break of the respective mixtures. The effect of such small amounts of accelerators on the elongation of vulcanized mixtures has already been commented upon in our previous article. In contradistinction to Stevens' view, we do not regard the composition of a mixture as fixed when different accelerators are used, even if they are employed in amount less than 1 per cent on the rubber.

Table II—Tests on Rubber No. 444

Accelerator	Accelerator Per cent	Sulfur Coefficient Actual	Sulfur Coefficient Excess	Load in Hectograms per Sq. Mm. to Effect Extension 1 to 7 Actual	1 to 7 Excess	1 to 8 Actual	1 to 8 Excess	1 to 9 Actual	1 to 9 Excess
Extra Light Magnesia	Control	1.009	...	0.53	....	0.67	....	0.78	....
	0.10	1.482	0.473	1.55	1.02	2.08	1.41	3.44	2.66
	0.25	2.117	1.108	2.75	2.22	4.42	3.75	8.01	7.23
	0.50	3.132	2.123	3.88	3.35	7.09	6.42	13.08	12.30
	0.75	3.440	2.431	5.11	4.58	8.97	8.30	16.65	15.87
	1.00	3.552	2.543	5.14	4.61	8.37	7.70	16.69	15.91
Accelerator A	Control	1.009	...	0.53	....	0.67	....	0.78	....
	0.10	1.678	0.669	1.49	0.96	2.04	1.37	3.21	2.43
	0.25	2.317	1.308	1.95	1.42	2.53	1.86	4.41	3.63
	0.50	2.938	1.929	2.20	1.67	3.05	2.38	4.62	3.84
	0.75	3.437	2.428	2.16	1.63	2.83	2.16	4.33	3.55
	1.00	3.685	2.676	2.40	1.87	3.19	2.52	4.64	3.86

In his second communication,[1] Stevens has drawn attention to the relationship between the coefficient of vulcanization and the load at a given extension. Our present results, for Samples 408 and 444, expressed in the same manner, are shown graphically in Fig. 2. It is at once evident in both cases that they differ markedly from the results obtained by Stevens. In the case of the mixtures which contained magnesia, the curves for both rubbers are practically straight lines up to coefficients of about 2.0 to 2.5, and, as Stevens has already noted, the excess load required to effect a given extension affords a fair measure of the rate of cure. In the case of Accelerator A, however, these curves are not straight lines, which shows that the load required to effect a given extension is not a measure of the rate of cure, as indicated by sulfur coefficients. Evidently, both rubbers vulcanize at almost the same rate when this accelerator is employed.

Both Stevens' and our own results are subject to the same interpretation. Our Accelerator A has been shown to decrease the load required to effect a given extension, *i. e.*, has increased the elongation as compared with extra light magnesia. It is quite possible, however, that Stevens' Accelerator I induced a greater resistance to extension under a given load than our Accelerator A. Furthermore, it is not entirely out of the question to select an organic accelerator which would actually increase the resistance to extension to more than that obtained with a similar quantity of extra light magnesia.

EXPT. III—A comparison was made of the results obtained with the two rubbers before and after extraction with acetone.

A 10-g. sample of the rubber was sheeted thin and extracted with acetone in a Soxhlet apparatus for 36 hrs. At the end of this time, the sample was dried *in vacuo* to constant weight and re-sheeted. The mixture was made by carefully sieving the required amount of sulfur and accelerator into the sheeted rubber and then rolling into a cylinder. The sample thus prepared was squeezed between the rolls of the mill to press the ingredients into the rubber without loss of either sulfur or accelerator. Subsequently, it was thoroughly mixed by re-sheeting and re-rolling until a homogeneous mix was obtained. After the samples had been allowed to age for 24 hrs. they were vulcanized in a button mold in the platen press and the combined sulfur estimated in the usual manner.

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[1] *Loc. cit.*, Fig. 3

Owing to the small size of the samples,[1] no physical tests were made.

The results of this experiment are shown in tabular form in Table III. It is seen that, despite the small size of the samples employed, the results obtained with the unextracted rubbers are in good accord with those previously found for similar quantities of the accelerator (Tables I and II). In the case of the extracted rubbers, however, this was not true.

TABLE III

	Sample 408				Sample 444			
	Unextracted Rubber		Extracted Rubber (Ext. 36 Hrs.) Acetone Ext. = 2.62		Unextracted Rubber		Extracted Rubber (Ext. 36 Hrs.) Acetone Ext. = 2.99	
	Sulfur Coefficient	Excess Coefficient	Sulfur Coefficient	Excess Coefficient	Sulfur Coefficient	Excess Coefficient	Sulfur Coefficient	Excess Coefficient
Control....	0.580	...	0.831	...	1.009	...	1.000	...
Extra Light Magnesia, 0.5 Per cent	1.874	1.294	1.290	0.459	3.132	2.123	1.343	0.343
Accelerator A 0.5 Per cent......	2.925	2.345	3.204	2.373	2.938	1.929	3.424	2.424

After extraction with acetone and vulcanization with the assistance of Accelerator A, Samples 408 and 444 were both found to have approximately (slightly higher) the same sulfur coefficients as were obtained with the unextracted rubbers, which have already been shown to be almost equal to each other. The extracted samples which were vulcanized with the assistance of extra light magnesia, however, gave entirely different results. Although the unextracted samples had sulfur coefficients of 1.874 and 3.132, respectively, the same mixtures, when prepared with acetone-extracted rubbers, had approximately the same sulfur coefficient, 1.3.

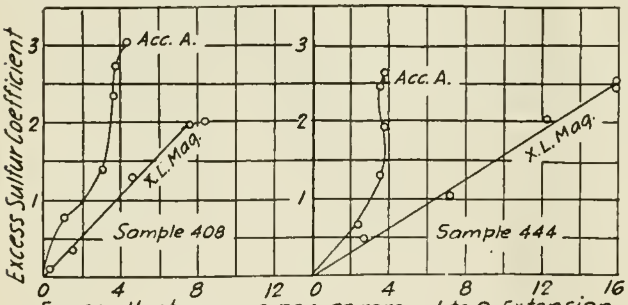

FIG. 2

It would appear that Sample 444 differed from Sample 408 quite markedly in the nature or condition of its acetone-extractable components. Although we recognize that the extraction with acetone may not be without effect upon the rubber or upon the extraneous substances left in the rubber, it would appear that, if the acetone-soluble substances are removed, not only is the response of the two rubbers to the accelerating influence of extra light magnesia decreased in both instances, but also the excess sulfur coefficients obtained are small and almost equal. The excess coefficients obtained were, indeed, so little above their controls that it would appear that a more complete removal of these extraneous substances would prove extra light magnesia to be almost inactive as an accelerator. As Accelerator A functions equally well with both rubbers, either before or after extraction, when judged on the basis of the sulfur coefficients obtained, the results obtained with it require no further comment. .

Final emphasis is placed upon the fact that all results were obtained with mixtures of rubber, sulfur, and accelerator only, and that the amounts of accelerators employed were small in all instances.

CONCLUSIONS

In view of the above experimental results, we are warranted in drawing the following conclusions:

I—The activity of small amounts of magnesia as an accelerator is largely of a secondary or contributory character, and acts in conjunction with, or obtains a response from, certain extraneous substances (probably nitrogenous) present in the rubber.

II—The activity of small amounts of magnesia is limited by the amount and nature of these extraneous substances originally present in the rubber.

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[1] It was obvious that the physical properties of the control mixture and the mixture which contained magnesia were very inferior to similar mixtures of unextracted rubber. This was not true, however, for the mixture which contained Accelerator A; the physical properties of this mixture were good and not greatly below a similar mixture prepared from unextracted rubber

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"PORCELAIN" WHITE LEAD

By Edwin Euston

EUSTON PROCESS COMPANY, SCRANTON, PA.

Received June 10, 1920

In the stack process of corrosion for the manufacture of white lead, two extreme results are noticed. Under properly balanced stack conditions the product is a dense "porcelain-like" crust, approximately $2PbCO_3.Pb(OH)_2$, but under less controlled conditions, such as occasionally exist in the top layer of a stack, the product is a light, fluffy powder, approximating $PbCO_3$. The characteristic appearance of the dense product has been assumed[1] as evidence that white lead is a definite compound, $2PbCO_3.Pb(OH)_2$, but this assumption does not account for the lack of coherence of the other compound.

An explanation is found in the relative cementing effect of the residual colloidal basic lead acetate in the "porcelain-like" crust, and of the residual normal lead acetate in the fluffy product. Probably because of the coarseness of particles, samples of commercial pulverized white lead, treated, respectively, with basic and slightly acid solutions of lead acetate and dried, do not demonstrate this difference in cementing effect; but the precipitation process for the manufacture of white lead affords full opportunity for the preparation of $2PbCO_3.Pb(OH)_2$ or $PbCO_3$ in very much smaller particles than the dried pulverized product. The cementing effect is then clearly shown, as the settled or filter-pressed $2PbCO_3.Pb(OH)_2$, when dried without previous washing, forms a hard "porcelain-like" mass extremely difficult to pulverize, the degree of hardness being proportional to the concentration of the basic lead acetate; but, when thoroughly washed before drying, forms a powder on slight pressure with the fingers. The $PbCO_3$ when dried without previous washing forms a cake noticeably softer than the unwashed $2PbCO_3.Pb(OH)_2$, and when thoroughly washed before drying readily forms a powder at a slight pressure. The particles of white lead when originally formed in the stack process are precipitates of fineness comparable to those of the precipitation process. The hardness of "porcelain" lead, therefore, is due not to its being an assumed definite compound, $2PbCO_3.Pb(OH)_2$, but to the cementing effect of the colloidal basic lead acetate present during formation of the crust.

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[1] Pp. 360, 361, and 364 of "Manual of Industrial Chemistry," edited by Allen Rogers. D. Van Nostrand Co., 1920.

UTILIZATION OF KID, RABBIT, HORSE, AND SEAL MEATS AS FOOD[1] [2]

By Arthur D. Holmes and Harry J. Deuel, Jr.
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Received May 12, 1920

The war emergency food situation led to a revaluation of foods with respect to nutritive value and use, including many which were not commonly known in the United States. This was true of meat products as well as of fats, cereal products, and other food staples.

The present experiments supply data regarding the digestibility of kid, rabbit, horse, and seal meats. Rabbit, both wild and domesticated, is a well-known food, used to considerable extent in some localities, particularly when the wild rabbit is in season. Kid is used in some localities in the United States, and horse meat is sold in some markets, particularly in large cities—a necessary requirement being that it be properly labeled. On the other hand, seal meat is unfamiliar to most Americans, although it is very commonly used as a food in the Pribilof Islands, the seat of the government seal fisheries. Although these meats are used only in a limited way in this country and its island possessions, large quantities could be made available for human consumption if there should be a demand for them.

EXPERIMENTAL PART

The methods followed in these experiments were essentially the same as those in previous ones of a similar nature conducted by this office.[3] The most satisfactory method of cooking the meat for this purpose was found to be in the form of small cakes, because this gave a uniform product that was easily sampled by cutting small sectors out of representative cakes. Very little difference in taste was noted in the cakes prepared from the different meats.

The purpose of these experiments was to determine the digestibility of the meat proteins, and the basal diet was so chosen as to supply a minimum of this food constituent. It consisted of bread, butter, fruit (orange), and sugar, with tea or coffee, if desired.

Young men, 20 to 40 years of age, students of a local university, were selected as subjects, the make up of the group varying somewhat during the different tests. All the men who took part in the experiment were familiar with this kind of work and were regarded as thoroughly trustworthy. So far as could be judged, all were in good health, of normal appetites, and fairly typical examples of normal young men in the prime of life.

The results of analyses of the meats studied are summarized in Table I.

As is evident from these figures, the several kinds of meat are similar in composition to others used as food.

TABLE I—COMPOSITION OF EDIBLE PORTION OF KID, RABBIT, HORSE, AND SEAL MEATS

Kind of Meat	Uncooked						Cooked					
	Water Per cent	Protein Per cent	Fat Per cent	Carbohydrate Per cent	Ash Per cent	Fuel Value per Pound Cal.	Water Per cent	Protein Per cent	Fat Per cent	Carbohydrate Per cent	Ash Per cent	Fuel Value per Pound Cal.
Kid	57.8	17.6	26.1	..	0.9	1342	44.8	38.8	11.5	...	3.8	1175
Rabbit	67.9	25.6	4.3	..	2.1	641	49.4	28.1	20.1	...	2.4	1330
Horse	....	....	....	..	...	....	64.5	28.6	4.1	1.3[1]	1.5	711
Seal shoulder (corned)	....	....	....	..	...	....	62.3	30.0	3.1	....	4.6	671

[1] Glycogen.

KID MEAT—The use of goat meat as a food is very old, and kid flesh has long been recognized as a desirable food by many races. However, contrasted with the results of studies by Sherman and Lohnes,[1] Bosworth and Van Slyke,[2] Jordan and Smith,[3] Hall,[4] and Hill,[5] to determine the dietetic value of goat's milk or some of its constituents, one finds in the literature little experimental evidence concerning the nutritive value of goat and kid flesh. In this country this is due, at least in part, to the relatively small consumption of these foods, which is largely limited to those of foreign birth or food habits.

Since it seems to be generally conceded that kid meat is preferable to goat meat, just as lamb is preferred to mutton, the digestibility of the flesh of a young animal was studied, such meat being obtained through the coöperation of the Bureau of Animal Industry. The entire fleshy portion of one-half of the carcass of a 6-month-old kid was removed from the bones, passed through a meat chopper, seasoned, thoroughly mixed, fried in the form of small cakes in a pan greased with a little lard, and served as a part of a simple mixed diet, in such quantity that it supplied the major part of the protein eaten.

The coefficients of digestibility for the entire ration, which on the average supplied 108 g. of protein, 111 g. of fat, 347 g. of carbohydrate, and 2,820 cal. of energy daily, were found to be 91.7 per cent for protein, 95.5 for fat, and 98.6 for carbohydrate. These values are in close agreement with those reported for the digestibility of the ordinary simple mixed diet, which are 92 per cent for protein, 95 for fat, and 97 for carbohydrate.[6] The digestibility of kid meat protein alone was estimated to be 94.4 per cent.

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[1] Prepared under the direction of C. F. Langworthy, Chief of the Office of Home Economics.

[2] Published with permission of the Secretary of Agriculture.

[3] U. S. Dept. Agr., *Bulletin* **310** (1915); *J. Agr. Res.*, **6** (1916), No. 16. *Ibid.*, **6** (1916), No. 17; U. S. Dept. Agr., *Bulletin* **649** (1918); **717** (1918), **761** (1919); **781** (1919).

[1] *J. Am. Med. Assoc.*, **62** (1914), 1806.

[2] N. Y. State Agricultural Experiment Station, *Techn. Bulletin* **46** (1915) 3; *J. Biol. Chem.*, **24** (1916), 173–175, 177–185, 187–189.

[3] N. Y. State Agricultural Experiment Station, *Bulletin* **429** (1917), 4

[4] *Ibid.*, **429** (1917), 7, Pop. Ed.

[5] *J. Biol. Chem.*, **33** (1918), 392.

[6] Connecticut Storrs Station, *Report* **1901**, 245

No attempt was made to obtain data regarding the digestibility of kid fat because that occurring in the meat was very thoroughly removed from the muscle tissue during the cooking process, and also because kid muscle fat mixed with kidney fat has been studied in another series of experiments and found to be 95.3 per cent digested.[1] On the basis of our results kid meat is apparently a very satisfactory source of protein that is well digested.

RABBIT MEAT[2]—For the purpose of these experiments rabbits (Belgian hare) believed to be representative of those procured by the average customer were purchased in the open market. The meat of wild rabbits was not available for study, but the digestibility should be about the same as that of the tame, because the two have practically identical chemical compositions, although they differ in appearance, the flesh of tame rabbits being lighter in color. The meat was prepared for serving by removing all the tissue from the bones, cutting in an ordinary household meat cutter, mixing uniformly, and frying into small cakes in a pan greased with a little lard. The rabbit meat contained very little fat and that present in the cakes was largely absorbed during frying.

On an average, the diet supplied 92 g. of protein, 114 g. of fat, 320 g. of carbohydrate, and 2,685 cal. of energy per man per day. The digestibility of the entire ration was found to be 90 per cent for protein, 95.8 for fat, and 97.9 for carbohydrate. Applying the usual corrections for the undigested protein present in the basal diet, it has been estimated that the digestibility of rabbit meat protein is 91.8 per cent. The subjects made no comment concerning their physical condition during the experimental period other than to state that they were in their usual normal health. The general conclusion obtained from these experiments was that rabbit meat is well assimilated and tolerated by the body.

HORSE MEAT—In this country relatively little horse flesh is used for human food. In Europe, however, it is a common article in the diet.[3] There is apparently little doubt that the supply of these animals will be sufficient to meet any probable demand in this country, for it is reported[4] that horses of "good flesh and health" but unsatisfactory for draft purposes on account of "wire cut," "over age," "inbred," and "under size" may be had from Montana ranches in carload lots.

A brief summary of information on horse meat as food, its qualities and identification, is included in a manual[5] prepared during the war for mess officers' use.

For the purpose of the experiments reported here a supply of meat was obtained through the courtesy of Mr. N. Hollister, superintendent of the National Zoölogical Park, from a normal healthy animal that passed rigid ante- and post-mortem inspections. In physical appearance the uncooked meat, though a deeper red in color, resembled beef very closely. To prepare it for serving it was passed through a meat cutter, seasoned, mixed uniformly, molded into cakes, and fried in a pan greased with a little lard.

On an average the diet supplied 126 g. of protein, 70 g. of fat, 349 g. of carbohydrate, and 2,700 cal. per man per day. Of the 126 g. of protein, 92 g. were derived from the horse meat, and this was found to be 96.4 per cent digested. No attempt was made at this time to determine the digestibility of horse fat, but in previous experiments the coefficient of digestibility was found to be 93.9 per cent.[1] In the reports of their physical condition during the experimental period, none of the subjects referred to any physiological disturbances resulting from the ingestion of a daily average of 306 g. of horse meat. It would accordingly appear that the protein of horse meat was both well tolerated and well utilized by the body.

SEAL MEAT—Under the supervision of the U. S. Bureau of Fisheries from 30,000 to 40,000 fur-bearing seals are slaughtered yearly. Though seal meat (seal shoulder) is used locally in the Pribilof Islands and is a well-known food of natives and explorers in the Arctic region, only a very limited portion of the amount furnished by the fur-seal fisheries has as yet been utilized, and as far as could be learned there is no experimental evidence on record concerning its digestibility. Records of Arctic travel, as for instance the observations of Stéfansson,[2] give much general information regarding seal meat and its uses, and from such data one can readily see that even if unknown elsewhere it has proved to be for uncounted time a valuable food of a very hardy people.

The seal meat used in these experiments was obtained through the courtesy of Mr. H. C. Fassett, specialist in charge of the fur-seal fisheries, and consisted of seal shoulders that had been packed in dry salt and later in brine. In preparing the meat for serving, it was soaked for 18 hrs. to remove salt, and boiled until tender. During both the soaking and the boiling, the water was changed two or three times. The cooked meat was removed from the bone, cut in an ordinary household meat chopper, seasoned, and cooked in the form of small cakes in a pan greased with a small amount of lard. In appearance and flavor the cooked meat very closely resembled corned beef.

Six digestion experiments were made with seal meat, but in two of them the data are not complete, since the tare for butter eaten as a part of the basal ration was overlooked. However, since the digestibility of protein was the primary interest, the experiments are reported without any allowance being made for the very small amount of protein supplied by the butter.

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[1] U. S. Dept. Agr., *Bulletin* **613** (1919), 7.

[2] A recent publication of the Department of Agriculture [*Farmers' Bulletin* **1090** (1920)] on "Rabbit Raising," summarizes some work of the Office of Home Economics on the composition of rabbit (Belgian hare) meat and the preparation and use of rabbits as food. Data are also given regarding the relation of live to dressed weight, the loss of weight in cooking, and the weight of bones and cooked meat.

[3] *Lancet* (London), **1** (1918), 189; *J. Am. Vet. Med. Assoc.*, *n. s.*, **4** (1917), 681.

[4] *Nat. Provisioner*, **58** (1918), 17.

[5] "Mess Officers' Manual," prepared by several officers of the Division of Food and Nutrition of the Medical Department, U. S. Army. Lea & Febiger, Philadelphia and New York, **1919**, p. 31.

[1] U. S. Dept. Agr., *Bulletin* **613** (1919), 12.

[2] Stéfansson, "My Life among the Eskimo," **1913**.

The subjects ate an average of 104 g. of protein, 79 g. of fat, and 338 g. of carbohydrate daily, an amount of food sufficient to supply 2,455 cal. of energy. Of the 98 g. protein consumed daily, the 69 g. derived from the seal meat were found to be 94.6 per cent digested. All the subjects except one reported that they were in normal physical condition during the experimental period; the one exception reported a tendency towards constipation at the termination of the period, a condition not infrequently resulting from diets that are very completely digested. The general conclusion to be drawn from these experiments is that seal-meat protein like that of other meats is well digested.

As is always the case in this experimental work, discussion of the food and ration is always avoided with the subjects. However, from conversation which was overheard, it was apparent that they did not note any unusual flavor and thought these meat cakes were "Hamburg steak."

SUMMARY

The results obtained in the digestion experiments with kid, rabbit, horse, and seal meats are summarized in Table II. The coefficients of digestibility there given for the protein, the fat, and the carbohydrate of the entire ration and for the protein of the meats alone are the averages of the coefficients of the digestibility obtained in the individual experiments with the different meats. The amounts of meat eaten are included as a matter of dietary interest.

TABLE II—SUMMARY OF DIGESTION EXPERIMENTS WITH MEATS

		Digestibility of Entire Ration				Amount of Meat Eaten		
Kind of Meat	No. of Expts.	Protein Per cent	Fat Per cent	Carbohydrate Per cent	Ash	Aver. per Man per Day Grams	Max. per Man per Day Grams	Digestibility of Meat Protein Alone Per cent
Kid......	3	91.7	95.5	98.6	87.9	163	166	94.4
Rabbit...	5	90.0	95.8	97.9	80.1	205	217	91.8
Horse....	7	94.3	94.5	98.5	83.2	306	414	96.4
Seal.....	6	91.9	92.9[1]	98.0[1]	88.2[1]	230	281	94.6

[1] Average of four experiments.

The total ration in all the tests was very well utilized—the carbohydrates, especially, being very completely absorbed, from which it is apparent that these meats did not decrease the digestibility of the other constituents of the diet. In every case the average amount of meat eaten daily was in excess of that included in the ordinary diet of the average person, and in no instance were any physiological disturbances noted. The digestibility of the protein of the four kinds of meat studied was essentially the same as that of other and better-known meats.

A CHEMICAL METHOD FOR THE DETECTION IN FRUIT OF A PRIOR FROZEN CONDITION

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Modern methods of cold storage of fruits sometimes raise the question whether too low temperatures have been employed, resulting in abnormal deterioration when the fruit is removed from storage. For example, pears are held at a lower temperature than peaches, and, if both are held at the same temperature, the peaches may be injured. The question arises whether fruit which has been frozen or only partly frozen can be distinguished from fruit not subjected to these low temperatures.

Extreme cases of frozen fruit can, of course, always be recognized after thawing by the mushiness and darkening of the pulp, by the modified taste, and by the rapidity of rot. Between the extreme frozen condition and the non-frozen condition, cases arise that cannot be judged by such obvious indications. Chemical and histological methods of examination suggest themselves for such cases.

CHEMICAL METHODS OF DETECTION

Before discussing chemical methods of detection it is necessary to have in mind the physical effects of ice crystals upon cells, as are fully described in the studies of Schander and Schaffnit.[1] These include progressive disintegration effects, such as the growth of ice crystals, the instreaming of water from adjacent cells, the concentration of cell saps, cell plasmolysis, the destruction of inner plasma membranes with attending loss of osmotic function, the infiltration of electrolytes, and the coagulation of the proteins of the protoplasm. From this description it may be concluded that such free mingling of materials can rapidly give rise to those products which are normally slowly formed by ripening and by over-ripening.

Changes in fruits after gathering are described by Otto and Kooper[2] as increasing the amount of invert sugar and producing losses of water, cane sugar, acidity, and nitrogen. Contino[3] observes a loss of pectin. Prinsen-Geerligs[4] observes conversion of starch to sucrose and decrease of acids. Tannic acid[5] appears and disappears. Many fruits lose water during ripening,[6] but the total water content may be increased by "metabolic water." The specific gravity[7] of good fruit increases on storing, while that of frozen fruit decreases. With apple after ripening and storage there is a slight increase in invert sugar followed by a continual decrease, and sucrose also gradually decreases.[8]

Since the concentrations of acids vary during ripening and over-ripening, their variation after freezing and thawing was considered as a possible means of detection of the prior frozen state. However, the work of Bigelow and Dunbar[9] indicated that the concentrations of acids are too low and the acids themselves too varied to be of value. Other components con-

[1] *Landw. Jahrb*, **52**, 1; *Chem. Zentr.*, **2** (1918), 397.

[2] *Z. Nahr. Genussm.*, **19** (1910), 10, 328.

[3] *Staz. sper. agrar. ital.*, **45**, 60.

[4] *Intern. Sugar J.*, **10** (1908), 372.

[5] Basset, *et al.*, *J. Am. Chem. Soc.*, **33** (1911), 416; *Science*, **33** (1911), 624; Tonegretti, *Staz. sper agrar. ital.*, **43** (1911), 369; Gerber, *Compt. rend.*, **124**, 1106; Behrens, *Centr Bakt. Parasitenk.*, **4**, Part II, 7770.

[6] Babcock, University of Wisconsin, *Research Bulletin* **22**, 87.

[7] Webber, *et al.*, California Agricultural Experiment Station, *Bulletin* **304** (1919), 245.

[8] Neidig, *et al.*, Idaho Agricultural Experiment Station, *Report* **1917**, 22.

[9] THIS JOURNAL, **9** (1917), 762. A full bibliography is given That the acid concentration may increase through rotting was shown by Hawkins, *Am J. Botany*, **2** (1915), 71.

sidered and abandoned were starch,[1] oxidases,[2] water,[3] nitrogen,[4] etc.[5]

That the changes in sucrose concentration could be used was suggested by such observations as the following: Sugars exercise the greatest protective action against freezing;[6] sucrose disappears in rotting fruit,[7] and is transformed to invert sugar during the stages of ripening and over-ripening; sucrose and invert sugar are differently localized[8] in the tissues of the fruit. The method described below makes use of the fact that freezing brings about a very rapid transformation of sucrose to invert sugar, the result, of course, of the free mingling of sucrose with inverting acids or invertase, or both.

METHOD OF ANALYSIS

One half of the fruit to be examined is analyzed directly and the other half is frozen with cracked ice and salt. Each sample of the fruit may be cut into halves, or, with very small fruit, two approximately equal samples may be set aside for the analysis. The directly analyzed portion involves the estimation of invert sugar before and after hydrolysis, yielding A and B; the frozen portion is also analyzed for invert sugar before and after hydrolysis, yielding C and D. In other words, the ratios of invert sugar to sucrose before and after freezing are compared.

In all cases the estimations are made by weighing the cuprous oxide formed after reduction. The respective solutions are measured out in triplicate in 10 cc. samples, treated with 10 cc. each of Fehling solutions I and II, diluted to a known volume (100 cc., for example), and boiled for a known time, say 5 min. The precipitates are filtered hot on weighed Gooch crucibles, washed with water and then with alcohol, and dried to constant weight at about 110° C. When the solutions are prepared in the manner described below no difficulty is met in filtering rapidly on the Gooch crucibles, and the first two analyses will usually agree.

SOLUTION A—The fruit is mashed in a mortar with water containing sufficient free alkali to maintain to the end an alkaline reaction, transferred to a flask or beaker, and boiled until a complete extract of the material is obtained. Since the percentage of invert sugar is not sought,[9] but only its ratio to sucrose, no weighing of fruit and maintaining of constant volumes need be made. A portion of the solution is filtered hot, then cooled and made slightly acid, and again filtered to separate colloids which would have a fatal effect on subsequent filtering. Enough solution is set aside for analysis (A) and the remainder is treated as follows:

SOLUTION B—A known volume of the solution is treated with a known volume of concentrated hydrochloric acid, estimated to be sufficient to hydrolyze the sucrose[1] when immersed in a boiling water bath for 20 to 30 min. After cooling and filtering, the solution is made alkaline, and analyzed for total reducing sugar, corrections for change of volumes being made in the final calculations.

SOLUTION C—After freezing[2] and thawing, the second half of the fruit is treated exactly as for Solution A.

SOLUTION D—This solution is prepared from C as Solution B is prepared from A.

A sound apple, frozen for 16 hrs., then thawed out and left standing for 24 hrs., was analyzed with the result indicated in Table I.

Table I

Solution	Sample (1)	Sample (2)	Average	Invert	Sucrose	Ratio	Percentage Inversion
A	0.1350	0.1370	0.1360	0.1360	0.1076	100 : 79.1	37.47
B	0.2435	0.2437	0.2436				
C	0.2282	0.2288	0.2285	0.2285	0.0863	100 : 37.7	
D	0.3166	0.3130	0.3148				

If the value 79.1 for sucrose is indicated by S, and the value 37.7 is indicated by *s*, the percentage of inversion (37.47) resulting from freezing (and thawing and autolysis to the time of analysis) can be calculated by the following, easily derived formula, in which the constant 1.052 is the ratio of molecular weights of two molecules of hexoses to one molecule of sucrose.

$$\text{Per cent of inversion} = \frac{10000\,(S - s)}{100\,S + 1.052\,Ss}$$

With other fruit, as, for example, the peach, similar changes resulted. The data in Table II were obtained with sound peaches frozen 12 hrs. and thawed 3 hrs.

Table II

Solution	Sample (1)	Sample (2)	Average	Invert	Sucrose	Ratio	Percentage Inversion
A	0.3095	0.3030	0.3063	0.3063	0.2313	100 : 75.51	12.00
B	0.5348	0.5385	0.5376				
C	0.1932	0.2228	0.2080	0.2080	0.1262	100 : 60.66	
D	0.3325	0.3358	0.3342				

Samples of this same supply of sound peaches analyzed 2 wks. later under the same conditions gave the following data:

Table III

Solution	Sample (1)	Sample (2)	Average	Invert	Sucrose	Ratio	Percentage Inversion
A	0.2266	0.2286	0.2276	0.2276	0.3184	100 : 139.9	8.93
B	0.5462	0.5459	0.5460				
C	0.2370	0.2368	0.2369	0.2369	0.2668	100 : 112.6	
D	0.5040	0.5034	0.5057				

Since the percentage of inversion here is only about three-fourths of that of the prior case (Table II), it is concluded that storage for 2 wks. produced one-fourth of the total inversion; in other words, freezing and thawing produced in 15 hrs. three times as much inversion as storage for 2 wks.

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[1] Neidig, Prinsen-Geeligs, etc., *Loc cit.* Some fruits, as for example, peaches, are practically devoid of starch.

[2] Gore, U. S. Dept. Agr., Bureau of Chemistry, *Bulletin* **142**, Yoshida, *J. Chem. Soc.*, **43**, 472; Bertrand, *Compt rend.*, **118**, 1215; Lindet, *Ibid.*, **120**, 370; Martinaud *Ibid.*, **121**, 512; Appleman, *Botan. Gaz.*, **50**, 182.

[3] Webber, *Loc. cit.*

[4] Bassett, *Loc. cit.*

[5] Windisch and Schmidt, *Z. Nahr. Genussm.*, **17**, 584.

[6] Maxinov, *Ber. botan. Ges.*, **30** (1912), 52, 293.

[7] Hawkins, *Loc cit.*

[8] DeMoussy, *Compt. rend.*, **161** (1915), 443. Acids and reducing sugars are expressed to the greatest extent with high pressure on the fruits, whereas non-reducing sugars are obtained with slight pressure.

[9] Knowledge of the concentrations of invert sugar and sucrose in the entire fruit is of no value in this connection since these vary with the variety and age of the fruit. The final per cent of inversion could be obtained on this basis, if so desired, but the method would be greatly complicated without yielding added value.

[1] For the hydrolysis of sucrose, see Wiley, "Agricultural Analysis," Vol. III, p. 105; Borntrager and Samelson, *Z. angew. Chem.*, **1892**, 334; **1893**, 690; **1894**, 267, 351; Munson and Walher, *J. Am. Chem. Soc.*, **28** (1906), 667.

[2] The freezing is conveniently made one day and the fruit set aside to thaw out during the night. The next day the analysis is begun and advantageously completed.

APPLICATION TO STORAGE FRUIT

Now, what changes can be expected in fruit first frozen in cold storage and then subjected to the foregoing methods of analysis? Evidently changes brought about by freezing in storage will not be repeated by a laboratory freezing, provided the first freezing was thorough and the laboratory freezing was not delayed too long. This was found to be the case with peaches alleged to have been frozen in storage, manifesting obvious characteristics of frozen peaches, and analyzed within a week after removal from cold storage (Table IV).

TABLE IV

Solution	Sample (1)	Sample (2)	Average	Invert	Sucrose	Ratio	Percentage Inversion
A	0.2595	0.2510	0.2555	0.2555	0.2550	100 : 99.80	1.26
B	0.5120	0.5090	0.5105				
C	0.2180	0.2170	0.2175	0.2175	0.2115	100 : 97.24	
D	0.4289	0.2293	0.4290				

Here only 1.26 per cent of inversion was obtained in the peaches by a laboratory freezing. Now, since unfrozen peaches (Tables II and III) gave much inversion by laboratory freezing, it may be concluded that the fruit analyzed in Table IV had previously been frozen in storage.

In this connection it may be observed that not only is sucrose inverted during ripening, over-ripening, rotting, and freezing, but invert sugar, previously present or formed by inversion, may be lost by chemical decomposition, or by the metabolism of the plant, or by rotting organisms, such as yeast or molds. This is illustrated by the following data obtained from peaches (Table IV) after they had been kept out of cold storage for one month and had become completely covered with mold.

TABLE V

Solution	Sample (1)	Sample (2)	Average	Invert	Sucrose	Ratio	Percentage Inversion
A	0.0735	0.0715	0.0725	0.0725	0.1325	100 : 182.76	30.01
B	0.2014	0.2086	0.2050				
C	0.1847	0.1735	0.1791	0.1791	0.1464	100 : 81.74	
D	0.3275	0.3235	0.3255				

It must be concluded that mold consumed a large part of the invert sugar, or at least that it consumed invert sugar more rapidly than it did sucrose. Therefore too great deterioration of fruit out of effective cold storage will invalidate the chemical detection of a prior frozen condition.

SUMMARY

The advantages of the method herein described are:

1—Advantage is taken of divergencies in the largest components of the fruit.

2—Inversion subtracts from the sucrose concentration and adds to the invert sugar concentration, thus giving accurate measurements of such divergencies.

3—Accurate gravimetric measurements are made by standard methods.

THE DETERMINATION OF MOISTURE IN BEET-SUGAR FACTORY PRODUCTS[1]

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The problem of obtaining the correct moisture content of various saccharine products is as important to the sugar laboratory chemist as is the knowledge of how to obtain correct data on the percentage of sugar or other constituents. He finds very definite and proved methods for the determination of sugar, alkalinity, ash, etc., in any standard reference book, but the literature is lacking in uniformity in regard to methods that prove experimentally to give correct results for the percentage of moisture.

ACCEPTED METHODS FOR MOISTURE DETERMINATION

The report of the editing committee of the Association of Official Agricultural Chemists gives the following method for the determination of moisture in massecuites, molasses, and other liquid and semi-liquid saccharine products.

DRYING ON QUARTZ SAND—Digest pure quartz sand with strong hydrochloric acid, wash, dry, ignite, and preserve in a stoppered bottle.

Place 6 to 7 g. of the prepared sand and a short stirring rod in a flat-bottomed dish, dry thoroughly, cool in a desiccator, and weigh. Add 3 to 4 g. of molasses, mix with the sand (if necessary, add a little water to incorporate the two thoroughly), dry in a water oven at the temperature of boiling water for 8 to 10 hrs., stirring at intervals of an hour, cool in a desiccator, and weigh. Stir, heat again for an hour, cool, and weigh; repeat the heating and weighing until the loss of water in an hour is not greater than 3 mg.

Pellet recommends that the material be mixed with pumice stone and dried at 102° to 105° C.

GERMAN OFFICIAL METHODS. THICK JUICE—A ratio of 25 parts of iron-free sand to one part of dry substance is sufficient. Three grams of thick juice to 50 g. of iron-free sand are weighed out. The drying takes place *in vacuo* at 105° to 110° C.

MASSECUITES—Two to three grams of massecuite are intimately mixed with 50 g. of iron-free sand in a moisture dish, and given a preliminary drying for a quarter of an hour in a drying oven at 70° C. After again thoroughly mixing, the drying is continued for 6 to 8 hrs. at 105° to 110° C. in a vacuum oven or air bath. The weight is taken as constant when, after repeating the drying for a period of 2 hrs., the loss in weight is less than 0.1 per cent.

PRESENT INVESTIGATIONS

Several years ago the writer did some work on methods for moisture determinations in beet-sugar factory products, and the results are submitted in the hope that they may furnish some information on the various factors influencing the determination of moisture.

As molasses is one of the most impure products with which we have to deal, it was used as a basis for most of the work, and the results were checked on purer products. It was assumed that the method that would give the highest results when using a temperature not above 110° C. was the most nearly correct. All our drying was done in an aluminium dish, 50 mm. in diameter by 30 mm. high, provided with a closely fitting cover.

The investigations covered the following points:

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[1] Presented at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

1—The result where the ratio of sand or other dividing material to molasses was kept constant, while the dividing material was varied in size.

2—The results with varying quantities of molasses and constant quantities of dividing material, and with constant quantities of molasses and varying quantities of dividing material.

3—The efficiency of various kinds of dividing material.

4—The effect of different temperatures of drying.

5—The effect of a short preliminary drying at a lower temperature, followed by a second mixing and a complete drying.

6—The uniformity of results obtained by drying in an ordinary bath at 105° C. as compared with drying in a vacuum oven at lower temperatures.

7—The amount of water or other liquid to add to the substance to give a homogeneous mixture.

8—The time required to mix the samples.

9—The meaning of the term "iron-free sand" as used in the German official methods.

FINENESS OF DIVIDING MATERIAL—It was found that the fineness of the material had a marked influence on the moisture driven off.

The sand used in this series of tests, as in all the rest of the work where sand was the dividing material, was a white sea sand that had been digested with hydrochloric acid, washed, and ignited. The first series of tests was with sand of four different sizes which were graded by passing through screens with circular perforations, *viz.*, coarser than 1 mm., between 1 mm. and 0.5 mm., between 0.5 mm. and 0.25 mm., and finer than 0.25 mm. The drying was done in an ordinary glycerol-filled, double-walled oven at 105° C.

The results of the investigation of this phase of the work are given in Table I.

TABLE I

Time of Heating Hrs.	Sand No 1 Coarser than 1 Mm. Per cent Loss	Max. Diff.	Sand No. 2 Between 1 and 0.5 Mm. Per cent Loss	Max. Diff.	Sand No. 3 Between 0.5 and 0.25 Mm. Per cent Loss	Max. Diff.	Sand No. 4 Less than 0.25 Mm. Per cent Loss	Max. Diff.
4	16.70	0.18	16.98	0.06	17.09	0.25	17.48	0.19
5	16.72	0.15	16.95	0.10	17.11	0.21	17.42	0.08
6	16.87	0.13	17.10	0.02	17.17	0.19	17.50	0.08
7	16.95	0.01	17.12	0.04	17.21	0.11	17.51	0.07
8	17.06	0.05	17.18	0.04	17.25	0.03	17.52	0.05
9	17.10	0.09	17.19	0.05	17.26	0.04	17.58	0.09
10	17.14	0.06	17.25	0.03	17.33	0.05	17.60	0.10
12	17.20	0.07	17.29	0.06	17.34	0.02	17.62	0.06
14	17.28	0.09	17.34	0.01	17.44	0.03	17.69	0.14
16	17.27	0.18	17.34	0.02	17.39	0.10	17.62	0.08
18	17.29	0.18	17.37	0.07	17.38	0.10	17.66	0.09
21	17.32	0.02	17.38	0.07	17.38	0.08	17.69	0.14
24	17.27	0.10	17.35	0.11	17.37	0.01	17.61	0.14
30	17.43	0.08	17.45	0.02	17.46	0.02	17.76	0.10
36	17.35	0.15	17.35	0.06	17.44	0.07	17.77	0.08
42	17.48	0.12	17.51	0.09	17.54	0.03	17.84	0.06
48	17.44	0.12	17.46	0.10	17.50	0.08	17.84	0.10

Briefly summarized, the results show that the finest of these sands gave the highest moisture content. The minimum time of heating any of the grades to obtain maximum results was 8 hrs. The loss in moisture at the end of this time on the fine sand was more than on the other grades at the end of the same period of heating by about 0.2 to 0.4 per cent, and the loss on the coarser grade never equaled that on the finer, even after 48 hrs. heating.

Later on, sand of 40 to 50 mesh, 50 to 60 mesh, 60 to 100 mesh, and finer than 100 mesh was tried out on another sample of molasses with the results shown in Table II.

TABLE II

MATERIAL	Time of Heating Hrs.	Sand No. 4 Less than 0.25 Mm. Per cent Loss	Sand No. 5 40 to 50 Mesh Per cent Loss	Sand No. 6 50 to 60 Mesh Per cent Loss	Sand No. 7 60 to 100 Mesh Per cent Loss	Sand No. 8 Less than 100 Mesh Per cent Loss
Molasses	4	17.65	17.46	17.58	17.66	...
	8	17.74	17.60	17.74	17.71	17.79
White Massecuite	8	7.63	...	...	...	7.62
Raw Massecuite	8	6.17	...	...	...	5.95
Thick Juice	8	37.44	...	...	...	37.31

From these results it was concluded that the sand must pass a 0.25 mm. screen to be suited to the work. The still finer grades are as satisfactory and may be used as a mixture containing all sizes from 0.25 mm. down. The grade used as a standard had the following composition:

40 to 50 mesh, 25 per cent
50 to 60 mesh, 25 per cent
60 to 70 mesh, 22 per cent
70 to 100 mesh, 22 per cent
Less than 100 mesh, 6 per cent

RATIO OF SAND TO MOLASSES—In both the above series, 25 g. of sand and 1 g. of dry substance were used. This ratio has been shown to be the one best suited to moisture determinations. The 25 g. samples gave as high results as the 30 or 35 g. An increase to 30 or 35 g. of sand is not objectionable, except that a larger dish than the one we used would be needed. In Table III are given the results of varying the amount of sand used with 1 g. of dry substance. Table IV, on the other hand, gives the results obtained when the amount of dry substance was varied.

TABLE III

Time of Drying Hrs.	15 G. Sand Per cent Loss	Max. Variation	20 G. Sand Per cent Loss	Max. Variation	25 G. Sand Per cent Loss	Max. Variation	30 G. Sand Per cent Loss	Max. Variation
4	16.98	0.04	17.61	0.07	17.48	0.19	17.23	0.12
5	17.44	0.04	17.61	0.04	17.42	0.02	17.75	0.14
6	17.38	0.04	17.64	0.03	17.50	0.08	17.62	0.07
7	17.45	0.01	17.67	0.04	17.51	0.07	17.69	0.10
8	17.55	0.01	17.61	0.09	17.52	0.05	17.63	0.15

TABLE IV

Time of Heating Hrs.	20 G. Sand Per cent Loss when 1 G. D. S. Used	25 G. Sand Per cent Loss when 1 G. D. S. Used	30 G. Sand Per cent Loss when 1 G. D. S. Used	35 G. Sand Per cent Loss when 1 G. D. S. Used
4	17.50	17.61	17.47	17.63
5	17.61	17.66	17.60	17.69
9	...	17.69	17.67	17.71
	Per cent Loss when 2 G. D. S. Used	Per cent Loss when 2 G. D. S. Used	Per cent Loss when 2 G. D. S. Used	Per cent Loss when 2 G. D. S. Used
4	17.44	17.48	17.51	17.49
5	17.50	17.54	17.56	17.55
9	17.53	17.54	17.61	17.67
	Per cent Loss when 3 G. D. S. Used	Per cent Loss when 3 G. D. S. Used	Per cent Loss when 3 G. D. S. Used	Per cent Loss when 3 G. D. S. Used
4	17.20	17.41	17.39	17.41
5	17.31	17.49	17.44	17.44
9	17.46	17.58	17.53	17.52
	When No Water Was Used in Mixing			
	Per cent Loss when 1 G. D. S. Used	Per cent Loss when 1 G. D. S. Used	Per cent Loss when 1 G. D. S. Used	Per cent Loss when 1 G. D. S. Used
4	17.13	17.63	17.62	17.40
5	17.33	17.63	17.62	17.52
9	17.42	17.67	17.69	17.60

EFFICIENCY OF DRYING MATERIAL—Sea sand, crushed quartz, and pumice stone were the only kinds of dividing material investigated.

The sea sand and crushed quartz gave identical results where the conditions of fineness and ratio of dry substance to sand were the same. The pumice stone was more difficult to manipulate and in all cases gave lower results in the same length of time of heating.

TEMPERATURE EFFECTS—The present work would indicate a temperature of 105° to 110° C. as the one best suited to drying sugar-house products. A temperature below 100° C. will not give maximum results in any reasonable time.

When trying the effect of a short preliminary drying at a lower temperature (70° C., as called for in the German methods) it was found that often, at the end of the 15 min. period of heating, the mixture had "set," so that a second mixing was impossible. The method did not seem to offer any advantages over the direct drying at 105° C., and increased the time of drying. The two following results on molasses are typical, where the total time of heating in both methods was 8 hrs.

	Sample	
	A	B
Our method, per cent moisture	21.88	17.78
German method, per cent moisture	21.36	17.55

The use of the vacuum oven to determine whether there might be some decomposition of the less stable constituents of beet molasses at the higher temperature did not indicate that any decomposition took place, and increased the time of drying. It required 18 hrs. to obtain the same results when drying under 17 in. of vacuum, at 80° to 83° C., as were obtained in 8 hrs. when drying at 105° C. in an ordinary oven.

The following tabulation is from one set of tests where 1 g. of molasses (dry substance) was used with varying amounts of sand.

	Grams of Sand			
	15	20	25	30
Moisture, in vacuum oven (18 hrs.)	17.61	17.34	17.54	17.67
Moisture, our method (8 hrs.)	17.55	17.61	17.66	17.67

AMOUNT OF LIQUID TO BE ADDED—No tests were made to determine the maximum amount of water that could be used. It was found that 1 cc. added to all of the heavier products containing 50 per cent or more dry substance gave a product that on mixing would occupy about 3 to 4 times the volume of the original materials. The mass in this condition was very porous and when dry contained many passages through which the moisture had escaped. When this amount of water was used there was no tendency for the sirup to leave the sand particles when the mixture was first heated. If too much water was added, the light, porous mixture was not obtained. A little experience will teach the operator when the proper condition is reached. Alcohol was substituted for water in a series of tests, but it gave no better results and offered no advantages.

TIME OF MIXING—The proper mixing of a sample requires from 3 to 5 min., and should be conducted in two stages. The sand, molasses, and water should be mixed for 2 to 3 min., then warmed on top of a bath for about 5 min., and given a second mixing for 1 or 2 min. When the time of mixing is less than above, there is often found in the dried mass small globules of the product that are not incorporated with the sand.

"IRON-FREE SAND"—The term "iron-free sand," as used in the German methods, apparently does not refer to sand that does not contain iron as one of its constituents, as the writer was unable to find either sand or quartz without at least traces of iron. It is evidently sand free from iron readily soluble in hydrochloric acid, and a series of tests made with mixtures of sand with metallic iron, ferric oxide, and magnetic oxide of iron indicated that in some cases the oxide of iron in small amounts reduced the moisture found. The results were erratic, but indicated that the sand used should be free from soluble iron.

	Sand + Fe_2O_3					
Sand Alone	0.25%	0.5%	0.75%	1%	1.25%	1.5%
79.25	79.03	78.98	79.24	79.02	79.05	78.98
	Sand + Fe_3O_4					
79.25	79.20	79.21	78.85	78.67		
	Sand + Fe (40 Mesh)					
...	79.16	79.35	79.17	79.27		

RESULTS FROM NEW METHOD—Samples of sand collected from nine laboratories, and prepared by sizing to finer than 0.25 mm. and washing and igniting, gave the following results. This series of tests was used as a measure of the uniformity of the dividing material as prepared under varying conditions.

Sand No.	Dry Substance in Molasses
1	79.06
2	78.92
3	78.78
4	79.04
5	79.13
6	79.06
7	79.20
8	79.05
9	79.03

With the exception of Sands 3 and 7, all the results are very uniform. All results given so far in this report were run in duplicate or triplicate and it was found very easy to check within 0.10 per cent on a duplicate determination. In nearly all cases, however, two sets of determinations, made on the same materials on different days, would not check. A difference of 0.20 per cent would often occur between duplicates run on different days. It was also found that the dried samples were very hydroscopic, and a gain in weight equivalent to 0.20 per cent moisture often occurred when the samples stood for 10 to 12 hrs. in a desiccator.

RECOMMENDED METHOD

In conclusion, these results are summarized in the following method, which is our standard as used at the present time.

Use only sand that will pass a screen with 0.25 mm. perforations; digest the sand in hot hydrochloric acid, wash, and ignite. Use 25 to 30 g. of sand, and dry and weigh just previous to making the determination. Weigh into the dish not over 1 g. of dry substance, add 1 cc. of water, place the dish on top of a drying oven until warm, mix for 3 min., and warm and mix again, until a perfectly homogeneous mixture is obtained. Dry at a temperature of 105° C. for 6 hrs., cool, and weigh. Repeat until the loss in weight after heating for a period of 1 hr. is less than 0.10 per cent.

Make all weighings as soon as the temperature of the desiccator is within 2° C. of the temperature of the balance. Repeat all determinations where the duplicates do not check within 0.20 per cent.

THE DETERMINATION OF NITRATES IN SOIL

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The analysis of soils for nitrate nitrogen is of considerable importance in connection with studies of the decomposition of farm and green manures and of the various factors controlling the production and accumulation of nitrates in soils. Nitrate nitrogen is recognized as the form of nitrogen preferred by most nonleguminous crops. In order to determine whether soils are properly meeting the crop demands for nitrate, systematic determinations of the nitrate nitrogen must be made under diverse conditions and especially in the presence of the growing crop.

During the last nine years nitrate studies involving many different conditions have been in progress in this laboratory. Five years' results of nitrate determinations on field soils have afforded excellent opportunity to study the value and accuracy of nitrate methods.

The method herein described has resulted from important modifications of the Devarda method. It has been applied on thousands of soil samples with excellent success. In principle, it depends upon the oxidizing action of sodium peroxide and the completeness of extraction of the nitrate with hydrochloric acid.

DETERMINATION OF NITRATE NITROGEN

The water-free samples from moisture determinations are placed in 400 cc. shaker bottles and 300 cc. of approximately 0.5 per cent hydrochloric acid are added. The mixture is then shaken in a mechanical shaker for 1 to 3 hrs. and allowed to settle over night. Five grams of sodium peroxide are placed in a 800 cc. Kjeldahl flask. A 200 cc. aliquot part of the acid soil extract is blown off into a graduated flask, then poured on the peroxide, and the contents of the flask boiled down to 20 to 25 cc., or, if urea is present, to complete dryness. Two hundred cc. of nitrogen-free distilled water are now added, together with 0.5 g. of Devarda's alloy (50 per cent aluminium, 45 per cent copper, and 5 per cent zinc), and the mixture distilled for 40 min., and collected in standard sulfuric acid. Sodium hydroxide of a strength such that 1 cc. = 0.5 mg. of nitrogen is used for titration. Rosolic acid or methyl red is the best indicator. A table of titrations reading direct to pounds per 2,000,000 lbs. of wet soil avoids laborious calculations.

NOTES ON THE METHOD

COLLECTION OF SOIL SAMPLES—From 24 to 30 borings are taken to a depth of 6.66 in. per 0.1 acre. These borings are placed in a 4-in. soil pan and carefully mixed. A composite sample is placed in a properly labeled glass fruit jar, to which 8 to 10 drops of toluene, or more, depending upon the amount of soil to be taken, have been added. The jars are then tightly sealed. Samples taken in this way may be shipped long distances without danger of bacterial changes that would affect the nitrogen. Samples without toluene were tested as to nitrate increase and found to have gained 10 lbs. in 2 days at normal moisture and to have lost all their nitrate when saturated.

DETERMINATION OF MOISTURE—One hundred grams of the thoroughly mixed sample are rapidly weighed into a seamless tin weighing box of 5 oz. capacity. Samples are dried in an electric oven at 110° C. for 10 to 14 hrs., then rapidly weighed. The loss on drying gives the per cent of moisture on a field basis. A table of factors is employed for referring the per cent to a water-free basis or to pounds per 100 lbs. of water-free soil. By moving the decimal point one place to the right for any figure reported on the water-free basis, tons of water per acre are obtained. Dividing the tons per acre by 113.25 tons expresses the results in equivalent inches of rainfall.

HYDROCHLORIC ACID EXTRACT—Hydrochloric acid was selected as the proper extractant for getting the nitrate out of the soil. It was thought that its action on colloids should cause the solution to settle with sufficient clearness to permit accurate analysis without filtration.

Hydrochloric acid was tested against sulfuric acid, acetic acid, water, sodium chloride, calcium and magnesium carbonates, calcium, magnesium, sodium and potassium hydroxide, calcium and magnesium oxides, and alum, and found to be the most efficient in removing the nitrate and yielding a clear soil extract.

A 0.2 per cent solution of the acid is very satisfactory where soils are not heavily treated with carbonates. The strength of the acid has not been found to affect the results within the limits of 0.2 and 1 per cent.

That the extraction of the nitrate with hydrochloric acid is complete, within a small error, is shown by a typical case represented below, where A represents the nitrate contained in the first extraction and B the nitrate contained in the second extraction:

$$B - \frac{A}{3} = 0$$

$$0.37 - \frac{1.15}{3} = 0$$

$$0.37 - 0.38 = -0.01$$

SODIUM PEROXIDE MODIFICATION—Sodium peroxide is used in place of sodium hydroxide for expelling ammonia and giving the required alkaline solution. By the use of this strong oxidizing agent the organic matter is destroyed at the same time, and hydrolysis of organic nitrogenous compounds during distillation with the metal is avoided. Sodium peroxide possesses the following advantages:

1—It gives a vigorous oxidation, although not a dangerous one, hydrolyzes the organic nitrogen, and expels the ammonia, leaving the required alkaline solution.

$$Na_2O_2 + 2HCl = H_2O_2 + NaCl$$

$$Na_2O_2 + H_2O = 2NaOH + O$$

2—It oxidizes to nitrate any nitrite present, and is without effect upon the ammonia or nitrate.

TESTS OF THE METHOD—Ammonia has been added to the soil both before and after extraction. It is always completely removed and does not influence the results. Nitrite has been added before and after extraction, and if present in large amounts will be lost because of the acid solution. Nitrates have been added before extraction, after extraction, and before reduction, and are always recovered within a very small experimental error. Tests for ammonia, made after boiling down to expel it and during the reduction with the metal, failed to yield any nitrogen. Amino acids, acid amides, urea and calcium cyanamide were introduced in the procedure to test the complete removal of the ammonia and to see if any organic nitrogen would be reducible by the alloy. The results proved that the nitrogen in the compounds, with the exception of that in urea and calcium cyanamide, was completely removed or rendered unreducible by the alloy. It was later found that nitrites present in the calcium cyanamide accounted for the apparent incomplete removal of nitrogen from that compound. For some unknown reason urea requires more complete boiling down than less easily hydrolyzable compounds.

TESTING FOR COMPLETE REDUCTION—Tests for nitrite and nitrate were made at various points in the procedure. Attention should be called to the fact that diphenylamine sulfuric acid cannot be used to test for nitrite or nitrate in the presence of any peroxide. In studying the completeness of the reduction it was found that the nitrates disappear in the first 5 min. of boiling. Ammonia did not accumulate sufficiently to give a test with Nessler's reagent which would read much above a blank. Nitrites persisted, however, for some 10 min. after boiling had started. A small amount of nitrogen was distilled after this time up to 40 min.

The metal is very rapidly spent, especially the aluminium and the zinc. Copper is left in extravagant quantities and is unable to effect a further reduction. It would seem that an alloy more highly compounded in aluminium and zinc, and with less copper would be as efficient and much less expensive. Five-tenths of a gram of alloy, all of which will pass a 20 mesh sieve, is used in this laboratory for most determinations of nitrate. If the quantity of nitrogen to be reduced is 25 mg., a gram of alloy should be used. Different lots of alloy vary widely in their reducing efficiency, a fact explainable on the basis of the differences in the degrees of fineness of different lots. The phenoldisulfonic acid, zinc-copper couple in acetic acid, iron-by-hydrogen, titanous sulfate, and aluminium reduction methods have been compared with the method herein described. The only one of these methods giving promise of being workable on a large variety of soils was the aluminium reduction method. Organic matter and possibly potassium aluminate greatly interfere with the rate of reduction if aluminium strips or aluminium powder are used. In one case with an ordinary soil it required 7 days in the cold before reduction was out of the nitrite stage in the aluminium reduction method.

CONFIRMATORY TEST WITH NITRON[1]—In order to determine whether all the nitrogen obtained by the reduction with Devarda's alloy was nitrate, a confirmatory method was sought. Precipitation of the nitrate with nitron in acetic acid solution offered the most satisfactory method.

A 10 per cent solution of nitron in 5 per cent acetic acid was used as the precipitant. One-tenth gram of nitron when treated with Na_2O_2 and reduced with the alloy gave no ammonia. Two typical soils were analyzed by the two methods.

	—Nitrate Nitrogen (Pounds per Acre)—	
Soil	Modified Devarda	Nitron Nitrate, Followed by Modified Devarda
1	55	57
2	270	277

A uniform acid soil extract was made up and analyzed as follows:

(1) 200 cc. by modified Devarda gave	12 mg. nitrate nitrogen
200 cc. by precipitation with nitron gave	0.3200 g. nitron nitrate crystals
0.3200 g. of nitron nitrate gave by reduction	9.5 mg. nitrate nitrogen
Filtrate from nitron nitrate gave by reduction	2.9 mg. nitrate nitrogen
Found	12.4 mg. nitrate nitrogen
Error based on modified Devarda	0.4 mg. nitrate nitrogen
(2) 200 cc. as above	12 mg. nitrate nitrogen
200 cc. by precipitation with nitron gave	0.3005 g. nitron nitrate crystals
0.3005 g. nitron nitrate gave by reduction	8.5 mg. nitrate nitrogen
Filtrate from nitron nitrate gave by reduction	3.5 mg. nitrate nitrogen
Found	12.0 mg. nitrate nitrogen
Error	0

The complete precipitation of the nitrate by nitron acetate in a weak hydrochloric acid soil extract is seriously interfered with by colloidal silicic acid. A water extract acidified with acetic acid while still in contact with the soil gives more satisfactory conditions for the precipitation of the nitrate with nitron solution. Even under the latter conditions precipitation is not complete, as seen from the above results. Organic matter and colloidal materials interfered with the precipitation under the conditions studied. It is evident that the nitron nitrate crystals contained impurities. Diphenylamine proved the presence of unprecipitated nitrate in the filtrate. The differences in the two methods are not large when the amounts of nitrate present in the soils are taken into consideration. From the results it is concluded that the modified Devarda method determines only nitrate nitrogen in the soil extract.

CONCLUSIONS

1—A method is described which involves important modifications in the Devarda method.

2—A modification of the method of extracting soils for nitrate determinations is reported in the use of a hydrochloric acid solution.

3—Sodium peroxide is used in place of sodium hydroxide. It serves to oxidize the organic matter and any nitrite that may be present. It yields an alkaline solution which expels the ammonia and leaves the proper condition for reduction with Devarda's alloy.

4—The method determines only nitrate nitrogen, as confirmed by precipitation of the nitrate in the soil extracts with nitron solution and the analysis of the crystals of nitron nitrate and the filtrate from the same.

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[1] Part of the nitron used in these experiments was made by the Division of Organic Chemistry, University of Illinois, Urbana, Ill

Slightly lower results are given by the Devarda method as herein modified than by the nitron method.

5—The method has been successfully used on thousands of soil samples representing varied conditions as to type and treatment. It has also been applied with satisfactory results to crop samples.

THE PROXIMATE ANALYSIS OF HARDWOODS: STUDIES ON QUERCUS AGRIFOLIA

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In previous papers[1] the author reported methods for the summative analysis of wood, and analyses of three coniferous woods and two hardwoods. It was shown that the procedure succeeded with the coniferous woods but not with the hardwoods. The present investigation was undertaken for the purpose of modifying the original scheme so as to make it applicable to the latter. Studies made upon one of the hardwoods (*Quercus agrifolia*), with which the original methods were unsuccessful, have resulted in a satisfactory accounting for the constituents of that wood. Further work is necessary to establish it as a method applicable to hardwoods in general.

The failure of the original scheme with the hardwoods was partly due to the fact that König's 72 per cent sulfuric acid method for lignin does not give reliable results with the woods of the broad-leaved trees. This has been observed by Johnsen and Hovey[2] as well as by the present author[3] and more recently by König and Becker.[4] These last authors have made a comparative study of König's sulfuric acid method, the 42 per cent hydrochloric acid method of Willstätter,[5] and a method of treatment with gaseous hydrochloric acid, as applied to woods. They found the three methods equally applicable to the coniferous woods, but with the hardwoods the hydrochloric acid methods alone gave the full yield of lignin. The gaseous hydrochloric acid method was recommended by these authors for the broad-leaved woods.

It appeared probable that the methods used previously for the analysis of the coniferous woods might be advantageously applied to the hardwoods, with the substitution of the newer method for lignin. Experiments were accordingly conducted with the object of working these out with the hardwood mentioned. In addition to the changes made in the lignin determination, attention has been given to the possibility of the presence of constituents not found in the coniferous woods.

PREPARATION OF MATERIAL

The material used in this investigation was the wood of coast live oak (*Quercus agrifolia*) in the form of fine sawdust. A sound branch about 5 in. in diameter was obtained, the bark removed, and cross-sectional cuts made by a fine saw (13 teeth to the inch) until the quantity of sawdust amounted to about 150 g. The sawdust was sifted through a sieve having 50 meshes to the linear inch. The oversize was dried at 100° C. for several hours, after which it was ground to pass through the 50 mesh sieve. The entire material was then well mixed and preserved in a screw-top Mason fruit jar to avoid changes in moisture content.

It was the intention at the beginning of this work to use the same analytical methods as were employed previously for the coniferous woods, with the single exception of the method for lignin. It was soon discovered, however, that simple extraction with benzene and alcohol did not produce a complete purification of the wood tissue from adventitious substances, as shown by the formation of a brown solution on washing with cold water, preliminary to chlorination. The use of the former procedure was objectionable in that it afforded no means of estimating the water-soluble constituents, which would accordingly not be accounted for in the summation. Furthermore it was found, as will be shown later, that this wood, when extracted with benzene and alcohol only, gives unsatisfactory results, as to yield and quality of product, in both the cellulose and lignin determinations.

The method finally adopted to overcome these objections was that of following the benzene and alcohol extractions with successive digestions in cold water and cold dilute sodium hydroxide solution. That redwood cellulose is unaffected by this treatment has been pointed out by the author.[1] Oak cellulose is similarly resistant.

ANALYTICAL METHODS

Methods for determining loss on drying, benzene extract, and alcohol extract are identical with those previously described in the case of coniferous woods.[2]

SOLUBLE IN COLD WATER—The residue from the alcohol extraction was dried, transferred to a 250 cc. beaker, 200 cc. of cold water added, and the mixture allowed to digest for 24 hrs. It was then filtered off on a tared Gooch crucible provided with a filtering disk of mercerized cotton cloth, washed, dried for 16 hrs. at 100° C., and weighed in a glass-stoppered weighing bottle. The difference between weights gives the residue after water extraction. The amount soluble in cold water is calculated by adding together the percentage figures for loss on drying, benzene and alcohol extracts, and residue after water extraction, and subtracting this sum from 100 per cent.

SOLUBLE IN COLD 5 PER CENT SODIUM HYDROXIDE SOLUTION—The residue from the water-soluble determination was transferred to a suitable beaker, and 100 cc. of 5 per cent sodium hydroxide solution were added. The mixture was left for 24 hrs., then filtered off upon the same Gooch crucible as before. It was washed thoroughly with water, several times with dilute acetic acid, and finally with water. After drying for 16 hrs. at 100° C. it was again weighed. The loss in weight from the previous weighing represents material soluble in cold 5 per cent sodium hydroxide solution.

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[1] This Journal, **11** (1919), 556; **12** (1920), 264, 476.

[2] *Paper*, **21**, No. 23 (1918), 36; also *J. Soc. Chem. Ind.*, **37** (1918), 132*t*.

[3] This Journal, **11** (1919), 562.

[4] *Z. angew. Chem.*, **32** (1919), 155; through *J. Soc. Chem. Ind.*, **38** (1919), 530*a*.

[5] *Ber.*, **46** (1913), 2401; through *Chem. Abs.*, **7** (1913), 3412.

[1] This Journal, **12** (1920), 268.

[2] *Ibid.*, **12** (1920), 477.

CELLULOSE—Cellulose was determined upon the residue from the above successive treatments. The analysis was carried out by the Sieber and Walter method previously described by the author.[1]

LIGNIN—For this determination the gaseous hydrochloric acid method of König and Becker was employed, with slight modification. The method proposed by these authors consists in adding 6 cc. of water to 1 g. of the wood (previously extracted with benzene and alcohol) in a test tube, then passing gaseous hydrochloric acid through the mixture until it is thinly liquid, in the meantime cooling the tube by immersion in ice. In the present investigation the wood was moistened with ordinary concentrated hydrochloric acid instead of with water. Excessive evolution of heat was thereby avoided, and cooling by simple immersion in water was found sufficient.

Four samples were run at the same time. Amounts of 1 g. each were subjected to the same purification treatment as for the cellulose determination, transferred to 1 × 10 in. test tubes, and treated with about 10 cc. of concentrated hydrochloric acid. The test tubes were closed with rubber stoppers, each containing two glass tubes for the introduction and exit of the gas. The inlet tubes extended nearly to the bottom of the test tubes. Hydrochloric gas, generated by dropping concentrated hydrochloric acid into strong sulfuric acid, was passed through the tubes containing the mixtures of wood and hydrochloric acid for about 2 hrs. The tubes were left closed for 24 hrs., then diluted, and the contents filtered on tared Gooch crucibles containing mercerized cotton cloth filtering disks, washed thoroughly, dried for 16 hrs. at 100° C., and weighed in glass-stoppered weighing bottles.

PENTOSANS NOT OTHERWISE ACCOUNTED FOR—The filtrates and washings obtained in four cellulose determinations were combined and evaporated to a little less than 1000 cc., transferred to a one-liter volumetric flask, and diluted to the mark. Aliquot portions of 125 cc. (= 1 g. of wood) were placed in the distilling flask of the pentosan apparatus, 30 cc. of concentrated hydrochloric acid added, and the furfural distilled off in the usual manner. The furfural was precipitated as phloroglucide, and the precipitate filtered off, washed, dried, and weighed. The results were calculated to pentosan by means of Krober's tables.[2]

The furfural-yielding constituents of oak are partly soluble in the alkali solution and most of the insoluble portion remains with the cellulose. The small amount unaccounted for with either of these proximate groups is found in the chlorination filtrates and washings.

MANNAN (RESIDUAL)—Ten grams of wood were dried, extracted with benzene and alcohol, and digested in water and 5 per cent sodium hydroxide solution as before, then hydrolyzed with hydrochloric acid (sp. gr. 1.025), and the mannan determined by precipitation as mannose phenylhydrazone. The details of the method have been described in a previous paper.

An attempt was made to determine total mannan by direct hydrolysis of the raw wood, but, owing to the interfering action of tannin or other substances dissolved from the wood, it was unsuccessful.

GALACTAN (RESIDUAL)—Five grams of wood were prepared as before, by successive extraction. The purified material was evaporated with nitric acid and the galactan converted into mucic acid by the method described for coniferous woods.[1]

FURFURAL AND METHOXY DISTRIBUTION—The methods used were those described in a previous paper.[1]

RESULTS OF EXPERIMENTS

The composition of oak wood as found by these methods is given in Table I. The figures are in every case averages of two or more determinations.

TABLE I—COMPOSITION OF LIVE OAK WOOD (*Quercus agrifolia*)

CONSTITUENT	Air-dry Basis Per cent	Oven-dry Basis Per cent
Loss on drying	4.20	..
Benzene extract	0.50	0.52
Alcohol extract	4.33	4.52
Soluble in cold water	3.66	3.82
Soluble in cold 5 per cent sodium hydroxide	18.71	19.53
Cellulose	45.48	47.47
Lignin	20.25	21.14
Pentosans not otherwise accounted for	1.89	1.97
Mannan (residual)	Nil	Nil
Galactan (residual)	1.49	1.56
TOTAL	100.51	100.53

In this table the first five groups of substances represent extraneous matter removed from the wood in the course of the purification process, while the last five groups represent substances contained in the residual purified tissue. The amounts obtained for each of the first five groups vary considerably with the manner in which the determinations are carried out, but the weight of purified residue remaining is in all cases about the same. In Table II the individual, as well as average values are given for constituents of the purified tissue, also for the yield of purified tissue.

TABLE II—COMPOSITION OF PURIFIED WOOD TISSUE

(Results in percentages of air-dry material, 4.20 per cent moisture)

	Individual				Average
Cellulose	45.33	45.04	46.19	45.38	45.85
Lignin	20.03	20.47			20.25
Pentosans not otherwise accounted for	1.80	1.98			1.89
Galactan (residual)	1.38	1.61			1.49
TOTAL					69.11
Residue after extraction (purified tissue)	68.80	68.50	68.86	68.22	68.60

The separate extracts obtained in the purification process have not been systematically examined. The benzene extract, consisting probably of oils and resins, is trifling in amount, as would be expected from the non-resinous character of the wood. The alcohol extract is a reddish brown material, consisting of tannin and possibly other coloring substances. The water and alkali solutions contain coloring substances not completely removable by alcohol extraction. In addition, the alkali solution contains a considerable amount of furfural-yielding groups. Two portions of the solution, on distillation with 12 per cent hydrochloric acid, yielded furfural corresponding to 11.47 and 11.11 per cent of pentosan. Two determinations of the acetic acid yielded by the raw wood upon hydrolysis with 2.5 per cent sulfuric acid gave 4.51 and 4.84

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[1] THIS JOURNAL, 12 (1920), 267.

[2] Browne, "Handbook of Sugar Analysis," Appendix, p. 83

[1] THIS JOURNAL, 12 (1920), 472.

per cent, after correction for formic acid by the method given in a previous paper.[1] The residue after digestion in sodium hydroxide solution yielded only traces of volatile acids. The series of treatments therefore removes the readily hydrolyzable acetic-yielding groups. It appears probable that the cleavage of acetic groups takes place during the alkaline digestion, rather than during the less drastic extractions that precede it. The alkaline extract could not be directly examined for acetic acid, because acetic acid had been introduced during the washing of the wood residue. The alkali-soluble portion probably consists chiefly of pentosans, substances yielding acetic acid upon hydrolysis, and tannin or other coloring substances.

To determine whether oak cellulose is injured by the treatments with cold water and alkali, cellulose determinations were made upon material so treated, and also upon material extracted with benzene and alcohol only. The products were examined by the mercerization test of Cross and Bevan.[2] The results of these experiments are given in Table III.

TABLE III—INFLUENCE OF WATER AND ALKALI DIGESTION ON YIELD AND QUALITY OF CELLULOSE

(Results in percentages of air-dry wood)

PRELIMINARY TREATMENT	No. of Chlorinations Required	Total Cellulose	α-Cellulose	β-Cellulose	γ-Cellulose
Extraction with benzene and alcohol only	9	46.18			
	8	44.79	29.38	10.08	5.33
	9	45.69	27.94	12.60	5.15
	8	44.23			
AVERAGE		45.22			
Extraction with benzene and alcohol and digestion in cold water and alkali	4	45.33	32.93		
	4	45.04	32.99	14.34	
	4	46.19	33.75		
	4	45.38	33.80		
AVERAGE		45.48			

It will be seen that the average of cellulose is practically the same in both cases, but the partly purified material requires much longer chlorination than that which was thoroughly extracted, in order to obtain a product equally free of lignin. The agreement of individual determinations is much better with the completely extracted material. The fully extracted material yields more α- and more β-cellulose than the partly extracted material, showing that, in the latter case, the excessive chlorination effects a partial degradation of the α-cellulose to lower forms. It was found difficult to obtain the β-cellulose in a form that could be filtered and washed. The single determination in the case of completely purified material is obviously inexact, as the sum of α- and β-cellulose is greater than the total cellulose. The results for α-cellulose, however, afford a reliable comparison of the quality of cellulose by the two processes, and show that a much better product is obtained when the alkali treatment is used.

The effect of the water and alkali treatment upon the lignin was also studied. Material completely extracted gave 20.03 and 20.47 per cent lignin. Material extracted with benzene and alcohol only gave on three determinations 22.11, 23.72, and 25.53 per cent of lignin. The latter results are variable and considerably higher than those on the completely extracted wood, due probably to the partial retention of substances soluble in sodium hydroxide solution but not in hydrochloric acid. Preliminary treatment with the alkaline solution is therefore essential to obtaining a pure lignin. The methoxy content of lignin is not changed by the alkaline digestion, as will be shown later in this article (see Table V).

A study of the distribution of the furfural-yielding groups in the wood gave the results shown in Table IV.

TABLE IV—DISTRIBUTION OF FURFURAL-YIELDING GROUPS IN OAK

(Results in percentages of air-dry wood, 4.20 per cent moisture)

	As Furfural			As Pentosan		
	Individual		Av.	Individual		Av.
Untreated wood	13.12	12.69	12.90	22.38	21.65	22.01
Completely extracted wood	6.84	6.82	6.83	11.71	11.68	11.69
Soluble in cold 5 per cent NaOH	6.71	6.50	6.60	11.47	11.11	11.29
Soluble in cold water	...	...	Nil	...	...	Nil
TOTAL (compare with untreated wood)	...	...	13.43	...	...	22.98
In cellulose	6.12	6.10	6.11	10.70	10.67	10.68
In chlorination solutions	1.15	1.05	1.10	1.98	1.80	1.89
In lignin	...	...	Nil	...	...	Nil
TOTAL (compare with completely extracted wood)	...	...	7.21	...	...	12.57

It will be observed that slightly more furfural was obtained from the fractions into which the wood was separated than from the wood itself. The same relation also holds with respect to the furfural yield from the fractions composing the completely extracted wood. The yield is variable, depending upon the conditions maintained during the analysis. By separating the material into several portions and subjecting each to the treatment prescribed for the pentosan determination, the opportunity for furfural production is extended, and increased yields are to be expected. With this explanation, the data in Table IV may be regarded as consistent.

The distribution of methoxy groups is shown in Table V.

TABLE V—DISTRIBUTION OF METHOXY GROUPS IN OAK

(Results in percentages of air-dry wood, 4.20 per cent moisture)

	Individual				Av.
Untreated wood	5.68	5.45			5.56
Wood extracted with benzene and alcohol	5.87	5.25			5.56
Completely extracted wood	4.43	4.36	4.21	(3.71)[1]	4.33
Lignin in wood extracted with benzene and alcohol	3.73	3.40			3.56
Lignin in completely extracted wood	3.53	(2.94)[1]			3.53

[1] Figures in parenthesis omitted from average.

The method and apparatus used gave good results with pure vanillin (20.35 per cent against 20.4 theoretical). Considerable difficulty was experienced, however, in getting concordant results with wood and lignin. This is believed to be due partly to imperfect contact between reagent and material, and partly to losses incidental to the excessive manipulation required in preparing the necessarily small sample for the determination. While there is considerable variation between duplicate determinations, the data nevertheless indicate marked differences in the methoxy content of the different preparations.

DISCUSSION

The methods here applied to oak wood as a typical hardwood may be regarded as fulfilling the following requirements of a satisfactory procedure for a summative analysis:

(1) They account for practically all of the material of the wood. The sum of constituents is as close to

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[1] THIS JOURNAL, 12 (1920), 474.

[2] "Paper Making," 1916 Ed., p. 97; THIS JOURNAL, 12 (1920), 267.

100 per cent as could be expected with methods of this character.

(2) As compared with other procedures tried, maximum yields of cellulose and lignin are obtained, with a minimum of impurities or degradation products.

(3) Overlapping of constituents is avoided. The cellulose was found free from lignin. The studies of König and Becker have shown that the gaseous hydrochloric acid method gives a cellulose-free lignin. The galactan is determined by a method too specific to include either of these constituents. The other constituents are determined in separate successive extractions and cannot therefore overlap with the above "residue constituents."

(4) No substances of importance have been overlooked. In addition to constituents specifically named in the analysis, woods are known to contain in greater or less amount: acetic-yielding groups, furfural-yielding groups (pentosans, etc.), methoxy groups, cutin, pectin, nitrogenous substances, and ash. A brief consideration of the available data will show that these substances are largely accounted for in the fractions determined.

It has been shown that the groups yielding acetic acid on hydrolysis are wholly contained in the extracts removed in purifying the wood tissue. A study of the furfural distribution shows that the pentosans are fully accounted for, partly in the alkali-soluble portion and partly in the chlorination filtrates and washings. The balance of the furfural yield is from the cellulose. The methoxy distribution shows that these groups are largely associated with the lignin. Most of the methoxy groups that are not so associated are accounted for in the water- and alkali-soluble portions. A small amount (0.8 per cent), however, is apparently split off during the hydrochloric acid treatment, and this portion is unaccounted for in the sum of constituents. Cutin is absent, as shown by the complete solubility of the cellulose residue in 72 per cent sulfuric acid. Precise information is lacking as to the chemical nature of pectins and their occurrence in woods. It is known that pectin contains methoxy, and yields furfural on distillation with hydrochloric acid and mucic acid on evaporation with nitric acid. The presence of galactan, pentosan, and non-lignin methoxy groups in the residue may be taken as a possible indication of pectin. If so, it is largely accounted for in its above-mentioned decomposition products.

The purified wood tissue after successive treatments with the four solvents contains only a few tenths of a per cent of nitrogen and a similar amount of ash. Presumably these small quantities are distributed over the constituents cellulose and lignin. No considerable error can result from neglecting them altogether.

As has already been noted, the composition of the various extracts has not been fully worked out. In their aggregate, the amount of these extracts measures the total amount of adventitious substances, as distinguished from the wood substance proper.

The distribution of furfural-yielding groups shows that there are probably three forms of these substances present in oak wood: the pentosans soluble in cold, dilute, sodium hydroxide solution, the furfural-yielding constituent of the cellulose, and the comparatively small amount of pentosan, resistant to the alkali treatment but dissolved during chlorination. It would appear that the first of these is wood gum (xylan or araban), and the second oxycellulose. The last may be due to more resistant pentosan or to pectin. The simultaneous presence of galactan and methoxy groups not due to lignin suggests the latter.

The present investigation indicates that alkaline digestion is necessary for the best results with oak wood, and presumably with the hardwoods generally. From the work done so far, it would appear that the coniferous woods should be prepared without, and the hardwoods with, alkaline digestion. Further work is necessary to determine whether this rule is generally applicable. It appears probable that the method of alkaline digestion will be found effective with all highly colored woods.

SUMMARY

1—Methods previously used for the analysis of coniferous woods were investigated as to their applicability to the hardwoods. Oak wood, as a typical hardwood, was analyzed by suitable modifications of these methods, with the results herein presented.

2—The purification treatment employed for the tissue of coniferous woods (successive extraction with benzene and alcohol) was supplemented with digestion in cold water and cold 5 per cent sodium hydroxide solution. These treatments remove all adventitious substances, but do not injure either the cellulose or the lignin.

3—Lignin was determined by the gaseous hydrochloric acid method recently proposed by König and Becker.

4—The modified procedure conforms to the requirements of a satisfactory analytical scheme in that it accounts for all of the material of the wood, yields the maximum amount of main constituents free from impurities or degradation products, avoids overlapping of constituents, and overlooks no constituents of importance.

NITRATE CONTENT OF CERTAIN WATERS CONSIDERED BACTERIOLOGICALLY SAFE[1]

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The quantity of nitrate nitrogen permissible in a potable water has been the subject of much consideration and speculation. While every sanitarian has his own quantity standard upon which he bases his judgment as to the source and quality of a given water, each agrees that a large amount of nitrate nitrogen cannot be disregarded. Richards and Woodman[2] say, "In eastern America nitrates above 0.5 part per million would arouse suspicion, and above 5 parts per million would in most cases prove previous pollution." Booth[1] concludes from his investigation that, "if nitrates are present in water above one part per million, it may have an unwholesome source." Stoddart,[2] in an article published in 1893 on the interpretation of water analyses, maintains "that natural waters can, at most, contain but from 0.1 to 0.2 grain of nitrogen per imperial gallon" (approximately 1.4 to 2.8 parts per million) "from sources other than animal matter." Quoting from Rideal[3] we find, "Therefore a water which contains over 0.5 to 0.6 part of nitrogen, as nitrates or nitrites in 100,000, may be certified as dangerous." On the other hand, Kühl[4] contradicts these opinions, after working with certain types of denitrifying organisms, by saying, "The presence of nitrates in water is not an indication of contamination."

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[1] Presented at the 59th Meeting of the American Chemical Society St. Louis, Mo., April 12 to 16, 1920.

[2] "Treatise on Air, Water, and Food," 3rd Ed., 1911, p. 92.

DETAILS OF PROCEDURE

The present paper is a report of the nitrate-nitrogen findings of 808 (Wisconsin) waters which were found to be safe bacteriologically. The bacteriological standards were those adopted by the Treasury Department of the United States for drinking water supplied to the public by common carriers in interstate commerce. The samples were collected in sterilized glass-stoppered bottles from deep wells, shallow wells, springs, and rivers; iced; and shipped to the laboratory in special containers. Drilled wells were arbitrarily considered deep, while those dug and driven were classified as shallow. A sanitary survey of the source of the water was not made in any regular manner, and only fragmentary data given by the local health officer who collected the sample were available for comparison. No correlation of these data with the analytical results has been attempted. The nitrate nitrogen was determined by the phenoldisulfonic acid method of the American Public Health Association,[5] using 50 cc. of the sample for a determination. A complete list of analyses will not be included in this paper, but only such groupings as will give a fair idea of the quantities present.

In order to compare the results of these analyses with analyses of normal waters given by other investigators, a compilation of their respective results is given in Table I.

TABLE I

SOURCE	LOCATION	NITROGEN AS NITRATES P. p. m.	INVESTIGATOR
Spring	Adirondack Mts.	0.28	Mason
Watershed	Croton, N. Y.	0.08 to 0.209	Fuller
Well water	Hyde Park, Mass.	0.532	Mass. State Board of Health
Spring	Arlington, Mass.	1.25	Mass. State Board of Health
Fresh pond	Cambridge, Mass.	0.3	Mass. State Board of Health
Driven well	South Carolina	0.6	Richards and Woodman
Deep well	Texas	0.0	Richards and Woodman
Deep well	Lake Winnipeg	1.6	Richards and Woodman
New wells	Lyon, N. Y.	0.1	Booth
Well	Norwich, England	8.0	Thresh
Well	Alexandria, Va.	0.3	Clarke
Artesian well	Rocky Ford, Col.	0.13	Hillebrand
Spring	Webster Grove, Mo.	4.0	Hillebrand and Howard

In Table II are given the total results of analyses of 808 waters irrespective of source.

TABLE II

Nitrate Nitrogen P. p. m.	Number of Waters	Percentage
0.00– 1.0	475	58.8
1.01– 5.0	193	23.9
5.01–10.0	101	12.5
10.01–20.0	35	4.4
20.01–30.0	1	0.1
30.01–40.0	1	0.1
40.01–50.0	1	0.1
50.01–60.0	1	0.1

From these results it is seen that a water may be entirely safe bacteriologically and yet have exceedingly high nitrates. In fact in each of 140 of these waters there is enough nitrate nitrogen to prove previous pollution, according to the standard of one author quoted. Bacteriological examinations tell us nothing, therefore, of the past history of a bacteriologically safe water, nor do they tell us anything of any potential danger. In other words, a bacteriological examination can at most tell us only whether the water sample at hand does or does not exceed the standard in number of certain counts and types of organisms.

In Table III the analyses are grouped to show the nitrate-nitrogen findings as related to the source of the supply.

TABLE III

Nitrate Nitrogen P. p. m.	Number of Waters	Percentage
	SPRINGS (71 Waters)	
0.00– 1.0	35	49.0
1.01– 5.0	20	28.0
5.01–10.0	13	19.0
10.01–20.0	3	4.0
20.0+	0	0.0
	SHALLOW WELLS (250 Waters)	
0.00– 1.0	124	50.0
1.01– 5.0	60	24.0
5.01–10.0	46	18.0
10.01–20.0	17	6.8
20.01–30.0	1	0.4
30.01–40.0	0	0.0
40.01–50.0	1	0.4
50.01–60.0	1	0.4
	DEEP WELLS (446 Waters)	
0.00– 1.0	277	62.1
1.01– 5.0	111	24.9
5.01–10.0	42	9.4
10.01 20.0	15	3.4
20.01–30.0	00	0.0
30.01–40.0	1	0.2
	LAKES (28 Waters	
0.00–0.1	15	52.0
0.11–0.5	11	40.0
0.51–1.0	1	4.0
1.01–2.0	1	4.0
	RIVERS (13 Waters)	
0.00–0.1	7	54.0
0.11–0.5	5	38.0
0.51–1.0	0	0.0
1.01–2.0	1	8.0

It is to be seen that low values for nitrate nitrogen, up to 5 parts per million, are found in 87 per cent of the deep well waters, while even the shallow wells and springs show a similar low figure for nitrate nitrogen, in 74 and 77 per cent, respectively. In the results for lakes and rivers no high values for nitrate nitrogen are found.

SOURCES OF NITRATE NITROGEN

A question naturally arises as to the source of this large amount of nitrogen which is present as nitrate in some ground waters. If it is derived from unpolluted soil leachings, from niter beds, or from nitrogen carried down from the atmosphere by rain as nitrates, we should not be at all concerned. The Rivers Pollution Commission,[1] after examination of a large number of samples of rain water, found the mean amount to equal 0.32 p. p. m. nitrate nitrogen.

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[1] "Water Analysis and the Nitrogen Content of Water," *J. Am. Water Works Assoc.*, **2** (1915), 61.

[2] *Analyst*, **18** (1893), 293.

[3] "Water and Its Purification," 2nd Ed., **1902**, p. 202.

[4] "The Reduction of Nitrates by Denitrifying Bacteria and Its Importance in the Judgment of Waters."

[5] "Standard Methods of Water Analysis," **1917**.

Gale[2] says that no extensive beds of nitrates are to be found in the United States, but that small deposits occur in many places throughout the country, especially in certain caves. Nitrogen as nitrate occurs in the soil in varying quantities, depending upon the nature of the soil, as well as on the time of year, kind of crop, and amount of cultivation. In general, soil contains from 5 to 200 p. p. m. of nitrate nitrogen, though Headdon[3] found as high as 60,000 p. p. m. in certain brown spots in Colorado soil. No such soil has been found, to the author's knowledge, in any other locality in the United States. That the amount of nitrates varies with the depth at which the sample is taken is illustrated by the work of King and Whitson,[4] who found that soil under clover and oats showed, in p. p. m. of the dry soil, 23.39, 18.33, 9.47, and 7.9 for the first, second, third, and fourth foot of soil, respectively. That manure piles, cesspools, cesspits, privies, sewage, and in fact any decaying animal matter may yield enormous amounts of nitrogen as nitrates is a well-known fact hardly necessary to repeat.

That ground waters receive large amounts of nitrate nitrogen from the soil is not borne out by the work of Malpeaux and Lefort,[5] who found that nitrates plowed to a depth of 10 in. appeared at the end of 11 days in the top 3 in., and those plowed to a depth of 20 in. reappeared in one month in the top 3 in. They finally concluded "that the summer rains never carry the nitrates beyond the reach of the roots of plants." Aladjem[6] concludes that "in waterlogged soils," a condition obtaining in many water-bearing strata, "nitrates are decomposed." Ritter[7] states that nitrates are reduced by the nascent hydrogen formed in the decomposition of peat. Tkachenko[8] remarks that there was "little leaching of nitrates during the rainy periods, and this was not noticeable in any case below 25 to 50 cm." Mendelejeff[9] gives his opinion that nitric nitrogen loses its oxygen on penetrating into the earth. A careful study of wells[10] in the immediate locality in which Dr. Headden reported 60,000 p. p. m. nitrate nitrogen in the soil, previous to the appearance of the niter trouble, failed to disclose more than a trace of nitrates. That surface waters do not abstract much nitrate from the soil is shown by the invariably low nitrate content of rivers and lakes at all seasons of the year. However, by allowing rain water to drain down through 2 ft. layers of soil samples contained in percolating pots, Fraps[1] obtained 11 to 200 p. p. m. of nitrate nitrogen. It seems possible, therefore, that if a fissure should form in the subsoil at a depth of 2 or 3 ft., a ground water might be obtained which contained a large amount of nitrates derived from the surface soil. In any event, the water so obtained could not be considered safe. In this connection Stoddart[2] describes an experiment in which sewage containing cholera spirilla was passed through a nitrifying bed of coarsely powdered chalk, with the result that although the organic matter in solution was completely nitrified, the cholera spirilla could be detected in the effluent. That the character of the soil does not have much effect upon the quantity of nitrate nitrogen in the ground water is indicated by the fact that ground waters in every locality of the state, representing soil ranging from the sand and gravel types to the heavy black soil of the marshes, are found with less than 1 p. p. m. In more than 75 per cent of the counties the low figure for nitrate nitrogen is below 0.1 p. p. m. These facts also oppose the theory that there are mineral deposits of nitrates from which the nitrate nitrogen is derived.

The work of Willis,[3] confirmed by the following example, shows that a well may be potentially dangerous, although safe bacteriologically: Dug well, in basement of a hotel in a small Wisconsin village, protected from surface washings, but subject to possible pollution from outhouses; soil, sandy loam. The bacteriological examination showed no *B. coli*, only 4 bacteria growing at 37° C., and only 13 growing at 20° C., but the nitrate nitrogen was 60 p. p. m. Judged bacteriologically, this is an entirely safe water, yet there are few sanitarians who would not condemn the supply on the nitrate findings.

CONCLUSIONS

1—An excessive quantity of nitrate nitrogen is not a normal component of safe ground waters.

2—Many difficulties must be surmounted before it will become possible to set an accurate standard, but from the results here presented and from the evidence contained in the literature, a water containing 5 or more p. p. m. of nitrate nitrogen should be considered as a potentially dangerous supply until a sanitary survey can be made by a competent person.

3—The nitrate-nitrogen determination should be included in every ground-water examination.

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[1] John C. Thresh, "Water Supplies," 2nd Ed., p. 166.

[2] U. S. Geological Survey, *Bulletin* **666**-Z.

[3] Colorado Agricultural Experiment Station, *Bulletin* **186** (1913).

[4] Wisconsin Agricultural Experiment Station, *Bulletin* **93**.

[5] "The Circulation of Nitrate in Soils," *Ann. Sci. Agron.*, **30** (2), 705.

[6] "Production of Alkali in Soils by Denitrification," *Cairo Sci. J.*, **8**, 274; through *Chem. Abs.*, **10** (1916), 3128.

[7] "Peculiarities of Nitrate Formation and the Nitrate Content of Moor Soils," *Intern. Mitt. Bodenk.*, **2**, 411; through *Chem. Abs.*, **8** (1914), 1180.

[8] "Observation on the Formation and Layer Distribution of Nitrates in Soils, with Different Nitrogen Fertilizers," *Khoziaistvo*, **37-40** (1912); *Zhur. Opytn. Agron.*, **14** (1913), 585; *Expt. Sta. Record*, **33** (1915), 422.

[9] "Chemistry," p. 223.

[10] Walter G. Sackett, "The Nitrifying Efficiency of Certain Colorado Soils," Colorado Agricultural Experiment Station, *Bulletin* **193**, 5.

[1] Texas Agricultural Experiment Station, *Bulletin* **171** (1914), 5.

[2] John C. Thresh, "Water Supplies," 2nd Ed., p. 167.

[3] "Value of Nitrate Figure in Determining Fitness of Water for Drinking Purposes," *J. Proc. Roy. Soc. New S. Wales*, **45**, 408.

RELATIONSHIP OF HYDROGEN-ION CONCENTRATION OF NATURAL WATERS TO CARBON DIOXIDE CONTENT[4]

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The effect of hydrogen-ion concentration upon biological processes has recently been much studied by biologists. The results indicate that it is more of a governing factor than is the total acid or alkali content.

[4] Presented at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

Illustrations are found in the fact that the limiting H^+-ion concentration of bacterial growth is as characteristic of each species as most other general tests, and that fresh-water and marine flora are found to vary with changing H^+-ion concentration.

Few data are available concerning the H^+-ion concentration of natural waters. Complete data concerning the carbon dioxide and carbonate content of waters are, however, often available, and may be used as a basis for the calculation of the H^+-ion concentration, since other salts or acids which would affect this value are rarely found in natural waters.

The following mass-law equations have been shown to be correct for carbonic acid:

$$\frac{(H^+)\ (HCO_3^-)}{(H_2CO_3 + CO_2)} = 3.0 \times 10^{-7} \qquad (1)$$[1]

$$\frac{(H^+)\ (CO_3^{--})}{(HCO_3^-)} = 6.0 \times 10^{-11} \qquad (2)$$[2]

Since most natural waters have a fairly high bicarbonate content and contain considerable free carbonic acid, Equation 1 should nearly approximate the conditions, for in the presence of appreciable amounts of both bicarbonate and free carbonic acid the ionization represented by Equation 2 would be slight. If, then, we have a record of the concentration of bicarbonate ion and of free carbonic acid, we can calculate the H^+-ion concentration.

According to "Standard Methods of Water Analysis," American Public Health Association, bicarbonate is determined by titration with 0.02 *N* acid, using methyl orange as an indicator. This value is, of course, that of the total concentration. It is probable that the bicarbonate is only about 85 per cent ionized. Free carbonic acid is determined by titration with 0.045 *N* sodium carbonate, using phenolphthalein as an indicator. The phenolphthalein end-point, under the conditions of titration, is obtained at a H^+-ion concentration of about 1×10^{-8}. Substituting in Equation 1, and solving for the amount of free carbonic acid, we obtain

$$(H_2CO_3 + CO_2) = 3.333 \times 10^{-8} \times (HCO_3^-) \qquad (3)$$

The free carbonic acid in the solution at the end of titration is a function, therefore, of the bicarbonate content, and is an appreciable quantity at all times. In Equation 1 we may therefore substitute the expression $(CO_2) + 3.333 \times 10^{-8} \times (HCO_3^-)$ for $(H_2CO_3 + CO_2)$, 85 per cent of the bicarbonate determined by titration for (HCO_3^-); and express the CO_2 determined as p. p. m. CO_2, and the bicarbonate as p. p. m. $CaCO_3$. The equation then becomes

$$(H^+) = \frac{4\ CO_2 \times 10^{-7}}{(HCO_3^-)} + 1 \times 10^{-8} \qquad (4)$$

If both bicarbonate and free carbon dioxide are expressed in terms of cc. of CO_2 per liter, or in terms of p. p. m. CO_2, Equation 4 becomes

$$(H^+) = \frac{3.5 \times 10^{-7}\ CO_2}{(HCO_3^-)} + 1 \times 10^{-8} \qquad (5)$$

The two equations offer a convenient means of calculating the H -ion concentration of any water for which the content of free carbonic acid and carbonates is known.

To check the accuracy of these calculations, several samples of water, from a variety of sources and varying widely in mineral and organic content, were examined. Bicarbonate and free carbon dioxide were determined according to "Standard Methods of Water Analysis." The free carbon dioxide titrations were continued to a faint pink which was persistent for 3 min. The H^+-ion concentration was determined colorimetrically,[1] using standard buffer solutions which had been checked by means of the hydrogen electrode. The results were expressed in terms of P_h^+, *i. e.*, the negative logarithm of the H^+-ion concentration.

TABLE I—COMPARISON OF CALCULATED H^+-ION CONCENTRATION WITH THAT DETERMINED COLORIMETRICALLY

SOURCE OF SAMPLE	Res. on Evap.	Free CO_2 P.p.m.	Bicarb. as P.p.m. $CaCO_3$	P_h^+ Det.	P_h^+ Calc.	Error
Drift Well..........	947	10.5	408	7.8	7.70	—0.10
	947	24.5	408	7.5	7.46	—0.04
	947	15.0	410	7.6	7.64	0 04
	947	34.0	409	7.4	7.35	—0.05
	947	12.0	408	7.8	7.66	0.14
Mine Water........	1172	0.0	292	8.0	8.00	0.00
	1172	7.0	291	7.6	7.71	0.11
	1172	9.0	292	7.6	7.65	0.05
	1172	14.0	293	7.4	7.44	0.04
	1172	23.0	292	7.4	7.40	0.00
Drift Well.	1573	10.0	352	7.6	7.66	0.06
	1573	16.0	353	7.5	7.54	0.04
	1573	24.0	352	7.4	7.40	0.00
	1573	25.0	354	7.4	7.40	0.00
	1573	26.0	352	7.4	7.40	0.00
Swimming Pool	446	1.0	96	7.8	7.85	0.05
	446	5.0	94	7.4	7.45	0.05
	446	6.0	90	7.4	7.43	0.03
	446	10.5	90	7.2	7.26	0.06
	446	22.5	90	6.8	6.95	0.15
Vermillion River....	375	0.0	154	7.9	8.00	—0.10
	375	7.0	152	7.5	7.54	0.04
	375	15.5	152	7.2	7.28	0 08
	375	16.5	152	7.1	7.29	0.19
	375	29.5	152	6.9	7.05	0.15
Vermillion R. Filtered	344	7.0	132	7.5	7.50	0 00
	344	22.0	130	7.0	7.10	0.10
	344	38.0	130	6.7	6.90	0.20
Shallow Well	459	4.0	376	7.9	7.84	—0.06
	459	4.0	374	8.0	7.84	0.16
	459	6.0	374	7.9	7.80	—0.10
	459	33.0	364	7.3	7.30	0.00
	459	35.0	362	7.3	7.30	0.00
Drift Well..........	328	7.0	218	7.6	7.62	0.02
	328	6.0	216	7.6	7.66	0.06
	328	16.0	214	7.3	7.38	0.08
	328	36.0	210	7.0	7.10	0.10
	328	38.0	210	6.9	7.05	0.15
Drift Well..........	330	7.0	224	7.8	7.64	—0.16
	330	9.0	222	7.7	7.57	—0.13
	330	21.0	216	7.3	7.32	0.02
	330	36.0	216	7.0	7.13	0.13
	330	43.0	214	6.9	7.00	0.10
Reservoir..........	280	1.0	74	7.6	7.80	0.20
	280	8.0	74	7.4	7.27	—0.13
	280	13.0	74	7.0	7.18	0.18
Reservoir Filtered...	254	5.0	64	7.4	7.38	—0.02
	254	14.0	64	6.9	7.00	0.10
	254	26.0	64	6.6	6.78	0.18
Kankakee River.. ..	384	6.0	100	7.3	7.47	0.17
	384	14.0	100	7.1	7.18	0.08
	384	25.0	96	6.7	6.94	0.24
Kankakee R Filtered	328	6.0	78	7.3	7.40	0.10
	328	17.0	80	6.9	7.02	0.12
	328	44.0	80	6.8	6.66	—0.14
Kankakee R. Filtered	230	16.0	28	6.3	6.62	0.32
	230	27.5	26	6.2	6.35	0.15
	230	37.0	28	6.2	6.24	0.04
	230	1.0	26	7.6	7.57	—0.03
Ohio River.........	206	15.0	44	6.9	6.83	—0.07
	206	29.0	44	6.5	6.52	0.02
	206	30.0	44	6.5	6.52	0.02
Mississippi River....	225	11.0	90	7.3	7.23	—0.07

Each sample of water was examined without modification and also after the addition of increasing amounts of water saturated with carbon dioxide. In taking the samples for titrations and for P_h^+ determinations, no special precautions were taken to prevent aëration. The results of 63 such determinations are given in Table I.

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[1] Landolt and Börnstein, "Physikalisch-Chemische Tabellen," p. 1132.

[2] Auerbach and Pick, *Arb. Kais. Gesundh.*, **38** (1912), 243.

[1] W. M. Clark and H. A. Lubs, *J. Bact.*, **2** (1917), 1, 109, 191.

In only one case was the difference between the determined and calculated P_h^+ greater than 0.3, and the mean variation is about 0.1. It will also be noted that the wider variations occurred in the cases of low bicarbonate content, which is to be expected from the assumptions made in the development of the equation. Somewhat larger variations are found in cases of high free carbon dioxide content than in similar cases with less carbon dioxide. This is probably due to the loss of carbon dioxide by aëration in the determination of both the carbon dioxide content and the P_h^+.

From their experiences with the colorimetric P_h^+ determinations, the authors do not feel that determinations can be made much more accurately than 0.2 P_h^+, using open tubes and ordinary methods of transferring the test sample to the tube. The effect of aëration of such unstable solutions as natural waters should amount to this much or more. It is advisable in all cases to make several determinations.

The formula cannot be applied to waters which are alkaline to phenolphthalein. An attempt was made to develop such an equation, but no waters naturally alkaline to phenolphthalein were available for checking the calculations. For unusual cases of this kind and cases of low bicarbonate content, it may be better to use some more complete and more complex equation, such as has been developed by Prideaux.[1]

CONCLUSIONS

Fairly accurate calculations of the H^+-ion concentration of natural waters can be made from the simple mass law equation of the primary ionization of carbonic acid.

Equations are developed for calculating H^+-ion concentration, in which the carbon dioxide and bicarbonate are expressed in the manner in which they are ordinarily determined. These equations are less accurate with low bicarbonate concentrations and do not apply to waters alkaline to phenolphthalein.

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A NEW TECHNICAL METHOD FOR THE ESTIMATION OF THE SACCHAROGENIC POWER OF DIASTATIC PREPARATIONS

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The most practical method for the estimation of the saccharogenic power of diastatic preparations is that of Lintner,[2] which is briefly outlined:

LINTNER METHOD

Separate volumes of 0.1, 0.2, 0.3, up to 1.0 cc., of 5 per cent diastase solution are added to a series of 10 test tubes, each containing 10 cc. of 2 per cent soluble starch solution. The tubes are allowed to incubate for one hour at constant temperature, at the end of which time 5 cc. of Fehling's solution are added to each tube, the liquids mixed, and the tubes immersed in a boiling water bath for 10 min. If, at the end of that period, the Fehling solution in the tube containing 0.1 cc. of diastase solution is just completely reduced, the diastatic power of the diastase is taken as 100. If 0.2 cc. reduces the 5 cc. of Fehling's solution, the diastatic power is 50, etc. More exact results may be obtained, if necessary, by taking 0.1, 0.15, 0.2, 0.25 cc., etc., of the diastase solution for a series of tubes, and determining more accurately the amount of digest which will just reduce 5 cc. of Fehling's solution.

The following formula is used for calculating the diastatic power of malt by the Lintner scale:

$$V : 0.1 = 100 : \text{diastatic power}$$

V is the volume of diastatic solution, 0.1 being the unit quantity used to make the value of 100 on the Lintner scale.

FAULTS OF LINTNER METHOD—This method has justly been criticized by Sherman and his associates:[1] first, as not being accurate, since there are only ten points on the Lintner scale at which an accurate determination can be made in the first operation; second, the probable error of the method increases rapidly with the diastatic power of the sample; if the end-point falls between the last two tubes (0.9 and 1.0 cc.) the diastatic power will be between 10 and 11.1, with a relatively small variation; but if it falls between the first two tubes (0.1 and 0.2 cc.) the diastatic power lies between 50 and 100, with a very large possible error.

The Lintner method can be further criticized as not easy or quick enough for technical purposes, particularly when a large number of tests have to be made as a routine in factory procedure. For example, to test 10 samples by the Lintner method, one has to use 100 test tubes, and different quantities of the diastatic solutions have to be tested 100 times at the definite intervals of time.

MODIFICATIONS OF METHOD—Ling[2] modified the Lintner method as follows:

A quantity of diastatic solution is added to 100 cc. of 2 per cent soluble starch solution in a 200 cc. flask, and kept at a constant temperature for one hour. At the end of this time, 20 cc. of 0.1 *N* sodium hydroxide are added and the solution is made up to 200 cc. with distilled water. After mixing, this solution is introduced into a buret and gradually run into 5 cc. Fehling's solution, diluted with a little water and kept boiling, until the solution just loses its blue color. If 25 cc. of the liquid (100 cc. of which correspond to 1 g. of soluble starch and 1.5 cc. of malt extract) are required to reduce 5 cc. of Fehling's solution, the diastatic power of the sample will be $\frac{100}{25 \times 1.5} = 26.7$.

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[1] *Proc. Roy. Soc. London* [A], **91**, 535.

[2] *Z. prakt. Chem.*, **34** (1886), 386.

[1] *J. Am. Chem. Soc.*, **32** (1910), 1075.

[2] Euler's "General Chemistry of Enzymes," **1912**, p. 290.

From practical considerations, this method also has various defects, chief among which are the slowness and inexactness of determining the quantity of sugar. There is no accurate agreement with the Lintner scale, since, by the method of Ling, the quantity of enzymes and production of sugar do not give an exact proportion; particularly is there a noticeable difference when the production of sugar is too much or too little. To obviate these difficulties, Sherman and his associates proposed a method which depends upon the gravimetric estimation of copper oxide. The method is, however, for that reason too troublesome for routine factory work.

PROPOSED METHOD

1—In the case of a solid sample, it must be first extracted with distilled water for 3 hrs. at room temperature. From 1 to 10 g. of the sample are usually extracted in 100 cc. of water. If the enzyme is too concentrated, the solution is further diluted with a known amount of distilled water.

2—Ten cc. of the extract or the diluted extract are put into a flask containing 100 cc. of 2 per cent soluble starch solution, which has been placed in a water bath kept at 40° C., the contents of flask are mixed, and the flask is allowed to remain in the bath for 30 min. At the end of that period, 10 cc. of 0.2 *N* sodium hydroxide are added at once to stop further enzymatic action.

3—Graduated quantities of the digest are then poured into a series of test tubes each containing 5 cc. of Fehling's solution; and the tubes are placed in a boiling water bath for 10 min., the tubes being shaken once during that period. The smallest quantity of the digested starch solution which just reduces 5 cc. Fehling's solution is determined. It may be more convenient to use at first only 2 or 3 tubes containing quantities of the digest within wide regions of variation, so as to determine the approximate concentration of the digest to be used. The reduction of the Fehling solution is then carried out within the narrow limits of this approximate value.

4—Knowing the amount of digested starch solution which will just reduce 5 cc. of Fehling's solution, we can calculate, as shown later, the Lintner value. The exact value is obtained by dividing the value found in the table by the percentage of the solid or liquid sample in the diluted enzyme solution.

CALCULATION TO LINTNER SCALE—Lintner's scale is very useful and popular; it was, therefore, found convenient to recalculate the values obtained by the new method in terms of this scale. An extract of a culture of *Aspergillus oryzae* (grown on bran) and an extract of malt were used in this investigation. The experiments were repeated numerous times so as to verify the results.

It was found that, with a definite extract of *Aspergillus oryzae* grown on bran, tested by the Lintner method at 40° C., 0.262 cc. of 1 per cent solution reduced 5 cc. of Fehling's solution. The following results were obtained by using the new method:

Strength of Extract Per cent	Vol. of Digest Required to Reduce 5 Cc. Fehling's Solution Cc.
4	3.5
3	4.0
2	5.0
1.5	5.75
1	7.5

In each case, 10 cc. of the particular concentration of diastase solution were added to 100 cc. of 2 per cent soluble starch solution, incubated for 30 min. at 40° C., then treated with 10 cc. of 0.2 *N* NaOH. The soluble starch was prepared according to Lintner, and its reaction so adjusted that 100 cc. of the 2 per cent solution required 0 to 1 cc. of 0.01 *N* NaOH to make it neutral with rosolic acid as an indicator.

By using the formula given by Lintner (on the Lintner scale), allowing for the concentration of the enzyme, we can calculate the value of the data obtained by the new method which would be comparable to those obtained by the original Lintner method.

$V : 0.1 = 100 :$ diastatic power (on Lintner's scale), since $V = 0.262$, when the concentration of the enzyme is not 5 per cent (as used by Lintner) but Y per cent, we find that:

$$\text{Diastatic power} = \frac{100 \times 0.1}{0.262} \times \frac{5}{Y} = \frac{184}{Y}$$

If $Y = 1$, then the diastatic value of the preparation used is 184 on the Lintner scale. The results of calculation to the Lintner scale are shown in Table I.

TABLE I—SACCHAROGENIC POWER SCALE FOR DIASTASE FROM *Aspergillus oryzae* (40° C.)

Obtained Value	Lintner Scale × Y	Obtained Value	Lintner Scale × Y
3.5[1]	735	10.5	126
3.75	643	11.0	120
4.0[1]	551	11.5	114
4.25	505	12.0	109
4.5	459	12.5	104
4.75	413	13.0	99
5.0[1]	367	13.5	94
5.25	336	14.0	89
5.5	305	14.5	84
5.75[1]	275	15.0	79
6.0	262	16.0[1]	69
6.25	249	17.0	65
6.5	236	18.0	61
6.75	223	19.0	57
7.0	210	20.0	53
7.25	197	22.0[1]	46
7.5[1]	184	24.0	42
7.75	178	26.0	38
8.0	172	28.0[1]	34
8.25	166	30.0	31
8.5	160	33.0	27
8.75	154	36.0[1]	24
9.0	148	37.0[1]	23
9.25	143	39.0	21
9.5[1]	138	45.0	19
9.75	135	50.0	17
10 0	132	...	...

[1] Experimental value.

This table can be used for every form of diastase originated from *Aspergillus oryzae*. If too much sugar is present in the diastase solution it is necessary to correct the obtained Lintner value by a blank test.

If the diastase is of different origin, the table may be changed somewhat since the course of digestion differs according to the enzyme.

The same procedure was followed to develop a scale for the diastase of malt, using an extract of powdered malt. This scale is shown in Table II.

Attention should be called here to the fact that the values falling between the experimental values were obtained by mere arithmetical calculations and not by mathematical interpolation. But, since this method is looked upon as a working factory method, the results

TABLE II—SACCHAROGENIC POWER SCALE FOR MALT DIASTASE (40° C.)

Obtained Value	Lintner Value × V	Obtained Value	Lintner Value × V
3.5[1]	735	10.5[1]	92
3.75[1]	551	11.0	89
4.0[1]	367	11.5	86
4.25	336	12.0	83
4.5	305	12.5	80
4.75[1]	275	13.0	77
5.0	262	13.5	75
5.25	249	14.0	73
5.5	236	14.5	71
5.75	223	15.0[1]	69
6.0	210	16.0	65
6.25	197	17.0	61
6.5[1]	184	18.0	57
6.75	177	19.0	53
7.0	170	20.0	49
7.25	163	21.0[1]	46
7.5	157	22.0[1]	44
7.75	151	24.0	40
8.0	144	26.0	36
8.25[1]	138	27.0	34
8.5	132	28.0	33
8.75	127	30.0	30
9.0	122	33.0	27
9.25	117	35.0[1]	23
9.5	112	36.0	22
9.75	107	39.0	20
10.0	102	45.0	18
...	...	50.0	16

[1] Experimental value.

are quite satisfactory. The best results are obtained by the use of 6 to 30 cc. digested starch solution (Lintner scale 200 to 30), which just reduce 5 cc. of Fehling's solution. Within these limits, the variation is rather small so that even the mere arithmetical averages are entirely satisfactory.

The following experiments will prove the adaptability of the new method for investigations of diastatic preparations.

(1) TIME EFFECT ON LINTNER VALUE—The influence of time upon the Lintner scale values obtained by the new method was determined. The results shown in Table III indicate that the Lintner value is practically proportional to the digestion interval.

TABLE III

Digestion Hrs.	Obtained Value Cc.	Lintner Scale	Time Factor	Lintner Scale × Time Factor
0.25	35.0	25	2	50
0.5	22.0	44	1	44
0.75	16.0	69	2/3	46
1.0	12.5	104	1/2	52
1.5	9.75	135	1/3	45
2.0	8.0	172	1/4	43

(2) TIME EFFECT ON SUGAR CONCENTRATION—The sugar content of the samples was determined at the end of 1 hr. The digested starch solution was kept for 48 hrs. protected with a cork stopper and the sugar content was determined again. (Further action of the enzyme, takadiastase in this case, was prevented by the presence of the alkali.)

TABLE IV

Samples	Obtained Value 1 Hr.	Obtained Value 48 Hrs.
A	35.0	35.0
B	22.0	22.0
C	16.0	16.0
D	12.5	12.5
E	9.75	9.75
F	8.0	8.0

(3) RELATION OF TIME TO AMOUNT OF DIASTASE—As shown in Table V, the quantity of diastase × period of digestion = constant. Takadiastase was used in the experiment.

TABLE V

	Duration of Digestion Hrs.	Obtained Value	Lintner Scale
Standard solution (10 cc.)	0.25	18.0	61
0.5 diluted solution (10 cc.)	0.5	18.5	59
0.25 diluted solution (10 cc.)	1.0	18.5	59
0.125 diluted solution (10 cc.)	2.0	19.0	57

EXPERIMENTS AT 50° C.—In many cases, 50° C. is used as the temperature of the enzyme action, since the digestion of the starch is more rapid and there is less change in slight differences in the temperature of digestion than there is at 40° C.

TABLE VI—SACCHAROGENIC POWER SCALE FOR THE DIASTASE OF *Aspergillus oryzae* (50° C.)

Obtained Value	Lintner Scale × V	Obtained Value	Lintner Scale × V
3.25[1]	952	12.75	81
3.5	833	13.0	79
3.75[1]	714	13.25	77
4.0	595	13.5	75
4.25[1]	476	13.75	73
4.5	429	14.0[1]	71
4.75	381	14.25	70
5.0[1]	333	14.5	69
5.25	311	14.75	68
5.5	289	15.0	67
5.75[1]	267	15.5	65
6.0	254	16.0	63
6.25	242	16.5	61
6.5	229	17.0	59
6.75	217	17.5	57
7.0	204	18.0	55
7.25[1]	191	18.5	53
7.5	178	19.0	51
7.75[1]	167	19.5	49
8.0	159	20.0	48
8.25	151	21.0	45
8.5[1]	143	22.0	42
8.75	138	23.0	40
9.0	133	24.0	37
9.25	128	25.0	35
9.5	123	25.5[1]	33
9.75[1]	119	26.0	33
10.0	115	27.0	32
10.25	112	28.0	30
10.5	108	29.0	29
10.75	105	30.0	28
11.0	101	32.0	26
11.25	98	34.0	24
11.5[1]	95	36.0	21
11.75	92	38.0[1]	19
12.0	89	40.0	17
12.25	86	45.0[1]	14
12.5	83	50.0[1]	10

[1] Experimental value.

Table VI has been worked out for 50° C. as the temperature of incubation.

TABLE VII—SACCHAROGENIC POWER SCALE FOR MALT DIASTASE (50° C.)

Obtained Value	Lintner Scale × V	Obtained Value	Lintner Scale × V
3.125[1]	666	9.5	96
3.25[1]	500	10.0	92
3.5[1]	333	11.0[1]	83
4.0	283	12.0	77
4.5[1]	233	17.0	71
5.0	199	14.0[1]	66
5.25[1]	182	15.0	62
5.5	173	16.0[1]	58
6.0	157	17.0	54
6.5	141	18.0[1]	50
6.75[1]	133	19.0	48
7.0	129	20.0	45
7.5	123	25.0[1]	33
8.0[1]	117	30.0	28
8.5	108	35.0[1]	23
9.0[1]	100	40.0	18
	...	43.0[1]	13
...	...	45.0[1]	12
...	...	50.0[1]	10
...	...	60.0[1]	7

[1] Experimental value.

CONCLUSION

The method outlined is very convenient for experimental studies on various diastatic products, such as malt and its various preparations, takadiastase, polyzime, etc. It is also convenient for the study of the influence of alkalinity, acidity, antiseptics, salts, etc., upon the activity of the diastatic preparation. The method has been used, as a routine factory procedure for over one year, with very good results.

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THE ANALYSIS OF AROMATIC NITRO COMPOUNDS BY MEANS OF TITANOUS CHLORIDE[1,2]

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Although considerable work has been done upon the determination of nitrogen in nitro compounds of the benzene series by means of titanous chloride, the method appears to be neither as well known nor as extensively applied as its merits deserve. This is probably attributable to the fact that a somewhat complicated apparatus is required, in addition to special care in the preparation of the standard solution, and analytical manipulation slightly out of the ordinary, especially in routine laboratories. These difficulties are, however, apparent rather than real, as it has been our experience, extending over a period of about three years, that the method satisfactorily meets the requirements of the research laboratory, where accuracy is of paramount importance, and of the control laboratory, where the time element is of almost equal weight.

The systematic application of this reagent to analytical chemistry is the result of the comprehensive researches of Knecht and Hibbert[3] on its application to the analysis of numerous types of reducible compounds, inorganic and organic, including a number of nitro derivatives of benzene and its homologs, as well as a few in the naphthalene series. It was the purpose of the present investigators to elaborate upon their work upon the aromatic nitro derivatives with a view to adapting their methods to the purposes of commercial control analysis. If this work lacks systematic coherence, it must be attributed to the fact that the prevailing conditions were such as to render it impossible to undertake the study as a fundamental research, the work being done fragmentarily to meet the demands of plant operation.

EXPERIMENTAL

In outline, this method depends upon the reduction of the nitro group to an amino group by treatment in a strongly acid boiling solution with an excess of standard titanous chloride solution. The excess is subsequently titrated cold with standard ferric alum solution, ammonium thiocyanate being used as indicator. As titanous chloride solutions are readily oxidized by atmospheric oxygen, the volumetric solution must be preserved under an inert gas, preferably hydrogen, and the analysis must be performed also in an innocuous atmosphere, most conveniently carbon dioxide.

STRENGTH OF STANDARD SOLUTIONS—Knecht and Hibbert[4] recommend an approximately 0.033 *N* solution of titanous chloride, the ferric alum solution being of about the same strength. Our experience has led to the adoption of two strengths of $TiCl_3$ solution, approximately 0.05 *N* and 0.25 *N*. The former is used for the estimation of small amounts of nitro compounds occurring in wash liquors, sludge cakes, etc., while the latter is employed in determining the purity of finished products. The stronger solution is preferable wherever it can be used without entailing an inconveniently large sample, as it yields more accurate results without in any way increasing the time of analysis. With both of these $TiCl_3$ solutions, a 0.05 *N* ferric alum solution is used, as experience has shown that this concentration combines speed, convenience, and accuracy.

PREPARATION OF STANDARD SOLUTIONS—In order that a stable solution may be obtained, due precautions must be observed in its preparation. In the first place, it is essential that the distilled water used be free from dissolved oxygen. The water is boiled for 20 to 30 min. and cooled in an atmosphere of carbon dioxide or hydrogen. Titanous chloride usually comes upon the market in 20 per cent aqueous solution. To prepare a 0.05 *N* solution, 33.5 cc. of the stock solution and 70 cc. of concentrated HCl (sp. gr. 1.19), for each liter of standard solution desired, are boiled together for about a minute. After cooling in an atmosphere of CO_2 or hydrogen, this solution is added to the previously prepared distilled water contained in the stock bottle in which it is to be preserved. Thorough mixing is obtained by passing a rapid stream of carbon dioxide or hydrogen through the solution. The 0.25 *N* solution is prepared similarly from 167 cc. of 20 per cent $TiCl_3$ and 150 cc. HCl per liter of standard solution.

It is essential that the concentrated titanous chloride solution and the distilled water be approximately at room temperature before mixing, as a high temperature in a dilute solution favors hydrolysis of the titanium compounds present, with the ultimate formation of a white precipitate, probably metatitanic acid, $TiO(OH)_2$. If such a sediment is noted in a standard solution, it should be filtered off at once through asbestos in a closed system, as this compound seems to catalyze further decomposition. For use in control laboratories, solutions may conveniently be prepared in 18 to 20 liter quantities.

The addition of about 50 cc. of carbon tetrachloride to the stock bottle containing the standard solution tends to absorb the trace of grease frequently present in distilled water, as well as that carried mechanically into the solution from the stopcock lubricant. The carbon tetrachloride has no apparent effect upon the utility of the titanous chloride solution and greatly decreases the frequency with which the buret must be cleaned, an operation somewhat inconvenient, owing to the connection of the top of the buret to the hydrogen reservoir over the standard solution.

The iron solution is prepared from ferric alum. Ferric chloride could probably be used equally well if obtainable in the pure state, but most of the C. P. $FeCl_3$ available contains relatively large quantities of ferrous salts which slowly oxidize, with consequent change in the relation between the iron and titanium solutions. For each liter of standard solution desired,

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[1] Presented at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

[2] This investigation was carried out in collaboration with Mr. H. G Tanner who was at the time connected with this laboratory.

[3] Their work has been published in the form of a monograph entitled "New Reduction Methods in Volumetric Analysis," Longmans, Green & Co., **1910**, reprinted with additions in **1918**.

[4] *Loc. cit.*, **1918**, p. 46.

24.2 g. of ferric alum are dissolved in water acidified with 50 cc. of 40 per cent sulfuric acid. The final solution should be free from ferrous iron, and may also be advantageously treated with carbon tetrachloride.

APPARATUS FOR STORAGE AND USE OF $TiCl_3$ SOLUTIONS—It has been found convenient to set up a 0.05 *N* and 0.25 *N* $TiCl_3$ solution and a 0.05 *N* ferric iron solution closely adjacent to one another, the last being between the other two. The solutions are connected to their respective burets by means of the usual siphon tube, in which, for accurate work, a thermometer should be placed. Another tube connects the top of the titanous chloride buret to the space above the solution in the stock bottle. This space is also connected to a small hydrogen generator. When the solution is in place and the system completely connected, the stopcock of the $TiCl_3$ buret should be turned to the delivery position, and a rapid stream of hydrogen allowed to pass through the apparatus for one-half hour or more to displace the air.

Where a large number of samples are to be analyzed, a large stock bottle of 40 per cent sulfuric acid may advantageously be placed on the same shelf close to the standard solutions. The siphon tube of this bottle should be fitted with a measuring tube roughly calibrated to deliver 25 cc. of solution.

As the analytical process is conducted under carbon dioxide, a carbon dioxide generator must be available. This apparatus, preferably of the Kipp type, is best charged with pink Tennessee marble, as experience shows that this material contains less occluded oxygen than the white Vermont variety.

The reaction is carried out in a 300-cc. Erlenmeyer flask provided with a tri-perforated stopper. Two of the holes serve for the entrance and exit of carbon dioxide, while the third accommodates the tip of the buret. To the exit tube is attached a 100-cc. flask serving as a trap to prevent air from being sucked back into the reaction flask on cooling.

STANDARDIZATION OF $TiCl_3$ SOLUTIONS—Knecht and Hibbert[1] recommend the standardization of the $TiCl_3$ solution by means of pure ferrous ammonium sulfate. A known quantity is titrated in H_2SO_4 solution to an exact end-point with dilute potassium permanganate, and the equivalent of ferric iron thus formed is then titrated in the cold with $TiCl_3$, with potassium thiocyanate or methylene blue as an indicator. The iron factor thus determined is calculated in terms of nitrogen.

Several objections may be raised to this procedure. In the first place, ferrous ammonium sulfate itself is not a desirable ultimate standard, especially for use in works laboratories, for, unless very carefully preserved, it is subject to oxidation and change in its water of crystallization content. Also, as a general principle, it is desirable to standardize a solution through as nearly as possible the same reaction and procedure as is to be used in the analysis, thereby automatically compensating for at least some of the inherent errors. It was found that in applying a 0.05 *N* $TiCl_3$ solution, standardized with ferrous alum, to the analysis of a pure nitro compound, the introduction of a correction of 0.3 to 0.4 cc. of $TiCl_3$ was necessary to obtain theoretical results. This "blank" was proved to be occasioned by extraneous oxidation resulting from atmospheric oxygen and possibly from other oxidizing agents in the reagents and the carbon dioxide. This extraneous oxidation does not occur to the same extent in the course of the standardization because it is run entirely at room temperature.

For these reasons, search was made for an aromatic nitro compound which would serve as a satisfactory ultimate standard. Fairly good results were obtained upon TNT (symmetrical, m. p. 80.78°), but this compound left much to be desired on account of its slight solubility in water and the inconveniently small sample demanded by its high nitrogen content. Its volatility with steam also jeopardizes its accurate use with the 0.25 *N* solution, where the sample required greatly exceeds the solubility of TNT in the reaction mixture. Consequently, some of the sample may be volatilized upon boiling before it can be reduced. *m*- and *p*-Nitroanilines, *m*-nitro-*p*-toluidine, and other nitro compounds are admirably suited to the purpose. The results given in Tables I and II indicate the accuracy with which standardizations may be accomplished, as well as the agreement that may be expected among results obtained with the various ultimate standards.

TABLE I—STANDARDIZATION OF 0.25 *N* $TiCl_3$ SOLUTIONS AGAINST *p*-NITROANILINE, TRINITROTOLUENE, AND *m*-NITRO-*p*-TOLUIDINE

Grams Nitrogen Found per Cc $TiCl_3$ Using		
p-Nitroaniline[1]	TNT	M. N. P. T.[1]
0.0005039	0.0005039	Standard Solution A
0.0005044	0.0005037	
0.0005042	0.0005039	
Av. 0.0005042	0.0005039	
Standard Sol. B	0.0005074	0.0005074
	0.0005069	0.0005075
	0 0005070	0.0005074
	0.0005073	0.0005077
	0.0005075	......
	Av. 0.0005072	0.0005075

[1] The melting points of the *p*-nitroaniline and M N P. T. samples used were, respectively, 148.7° and 115 3° C.

TABLE II—STANDARDIZATION OF 0.05 *N* $TiCl_3$ SOLUTION AGAINST FERROUS AMMONIUM SULFATE, TRINITROTOLUENE, AND *p*-NITROANILINE

Grams of Nitrogen Found per Cc. $TiCl_3$ Using		
Ferrous Ammonium Sulfate	TNT	*p*-Nitroaniline
0.00010495	0.00010443	0.00010441
0.00010493	0.00010453	0.00010445
0 00010494	0 00010453	0.00010449
0.00010491	0.00010464	......
0.00010495	......	......
Av. 0.00010494	0.00010453	0.00010445

The same samples of *p*-nitroaniline and TNT were used in this as in the previous case. The ferrous ammonium sulfate was purified by several recrystallizations from water and was free from ferric iron. It will be noted that the average factor obtained with this material is about 0.4 per cent higher than either of the other two factors. This is attributable to the extraneous oxidation being included in the TNT and nitroaniline factors to a greater extent than it is in the ferrous sulfate factor.

As *p*-nitroaniline is more readily available than *m*-nitro-*p*-toluidine, and is also more easily purified, it has been adopted as the ultimate standard in this laboratory. *m*-Nitroaniline is equally satisfactory.

The relation between the $TiCl_3$ and ferric iron solutions is established by boiling 50 cc. of the 0.05 N $TiCl_3$ solution or 25 cc. of the 0.25 N with 25 cc. of 40 per cent H_2SO_4 and 25 cc. of water or alcohol, cooling, and titrating with the iron solution exactly as described in carrying out the analytical process. As our experience has proved the necessity for strict adherence to apparently minor points of manipulation, this is described in detail below.

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[1] *Loc. cit.*, **1918**, p. 48.

ANALYTICAL PROCEDURE—Weigh a sample of the nitro compound containing 0.020 to 0.025 g. of nitro nitrogen. If the 0.25 N $TiCl_3$ solution is to be used, transfer the sample directly to a 300-cc. Erlenmeyer flask and treat with 25 cc. of water or alcohol, depending upon in which it is the more soluble. The sample should be completely dissolved, by gently heating, if necessary. If the 0.05 N solution is to be employed, dissolve the sample in alcohol, water or dilute acid, dilute to 250 cc., and transfer a 25-cc. aliquot part to the Erlenmeyer flask. From this point on, the procedure with either strength of standard solution is the same.

Add 25 cc. of 40 per cent sulfuric acid, connect the flask to the buret and, after sweeping for 5 min. with a rapid stream of CO_2, add 50 cc. of $TiCl_3$. Remove the flask, plugging the vacant hole with a glass rod, and maintain just at the boiling point for 5 min. During the boiling, the rate of passage of CO_2 may be greatly reduced. Cool the flask to room temperature or below by immersing in cold water, the flow of CO_2 being increased at this point to prevent the drawing of water from the trap back into the reaction flask. If the volume of solution has materially diminished, it should be diluted to approximately its original concentration with distilled water added through the stopper by means of a pipet. Connect the flask with the iron solution buret and titrate until the violet color of the $TiCl_3$ has been just discharged. Disconnect the flask and add through the stopper 10 cc. of 10 per cent NH_4CNS solution. Again connect the flask to the buret and continue the titration until a faint pink color, permanent for one minute, is obtained.

Since six equivalents of $TiCl_3$ are required for the reduction of one nitro group, one cc. of 0.05 N $TiCl_3$ is equivalent to 0.00011675 g. of nitrogen.

DISCUSSION OF ANALYTICAL PROCEDURE—The total time required for a determination, including weighing and aliquoting the sample, should not exceed one-half hour. By using two outlet tubes from the carbon dioxide generator, one sample may be swept out while another is being titrated, thus reducing the time somewhat.

The vital point in the determination is to be found in the excess of $TiCl_3$ used. It is absolutely essential for the complete reduction of the majority of the compounds studied that the final concentration of $TiCl_3$ after boiling be equivalent to about 25 cc. of 0.05 N $TiCl_3$ in a volume of 100 cc. A greater excess is in no way detrimental, but appreciably less is almost certain to result in incomplete reduction. In the case of the 0.25 N solution, the back-titer of iron solution should be in the neighborhood of 50 cc.

It is hardly necessary to state that oxidizing agents other than nitro compounds must not be present in the sample when analyzed. Among the interfering substances most frequently found in crude works materials may be mentioned ferric iron and nitrates.

In highly accurate work, it is essential that the reagents be as free as possible from dissolved oxygen. The water and alcohol (ethyl or a non-pyridine denatured) should be freshly distilled and preferably condensed in an atmosphere of CO_2. For control purposes, however, such precautions are unnecessary. If alcohol is used generally as the solvent, the standardization of the solution should be run with 25 cc. of alcohol instead of water, for unless the alcohol is very pure, a slightly different factor may be obtained. This point, also, need not be considered in plant work.

It will be noted that the details given above vary from those laid down by Knecht and Hibbert principally in the following respects:

1—Sulfuric acid has been substituted for hydrochloric acid because it has been found to contain less reducible impurity. It has also been noted that ferric chloride exerts an appreciable oxidizing action upon the thiocyanate indicator, this tendency being exhibited to a far less degree by ferric sulfate.

2—The period of boiling has been reduced to 5 minutes.

3—The practice of replacing the loss during boiling has been found advantageous, as the end-point varies somewhat with the concentration of the indicator. This variation becomes appreciable if the solution has become highly concentrated during boiling.

4—The ammonium thiocyanate indicator is added toward the end of the back titration, rather than at the beginning, to minimize the oxidation of the NH_4CNS by the ferric sulfate.

COMPOUNDS TESTED, AND RESULTS

The following are the more important nitro compounds specifically studied. In all cases they were analyzed with the 0.25 N $TiCl_3$ solution, following the procedure detailed above, unless otherwise specifically stated.

NITRO HYDROCARBONS—Mononitrobenzene, toluene, xylene, and naphthalene have received very little attention so far, as their analysis by this method was not sufficiently important from the works standpoint to warrant investigation. It was established, however, that they are not reduced completely when treated according to the standard procedure. Their analysis after previous sulfonation[1] has not been checked.

MONONITRO COMPOUNDS CONTAINING ADDITIONAL POSITIVE OR NEGATIVE GROUPS—The application of the method to *p*-nitroaniline has been described above, and the results obtained upon the *m*-isomer were equally satisfactory. The sample was purified by repeated crystallizations from water and melted at 112.5° C.

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[1] Knecht and Hibbert, *Loc. cit.*, p. 73.

o- and *p*-Nitrophenols (m. p. 44.8° and 113.2°, respectively), as well as their sodium salts, readily yielded quantitative results. *m*-Nitro-*p*-toluidine (m. p. 115.3° C.) gave very good results, the figures obtained upon the corresponding *o*-derivative (1-methyl-2-nitro-4-aminobenzene, m. p. 77.7° C.) indicating an equal degree of accuracy. Typical results on these compounds are given in Table III. The results obtained with various samples of 3- and 5-nitrosalicylic acids are also given.[1]

TABLE III—PERCENTAGE PURITIES OBTAINED FOR TYPICAL MONONITRO COMPOUNDS

m-Nitroaniline	*o*-Nitrophenol	*p*-Nitrophenol	*m*-Nitro-*p*-toluidine	*o*-Nitro-*p*-toluidine	5-Nitrosalicylic Acid		3-Nitrosalicylic Acid	
					M.P. ° C.	Pur.	M.P. ° C.	Pur.
100.00	100.09	100.07	99.92	100.01	234.5	99.97	145.3	99.72
99.92	100.08	100.00	99.93	100.05	230.8	99.89	145.6	99.87
100.03	100.15	99.95	100.10	100.03	230.5	99.92	144.8	99.02
100.00	100.10	100.15	99.90	100.05	228.6	99.93	145.5	99.73

From the above results, it seems that the introduction of either positive or negative groups into the nitrohydrocarbon molecule renders it susceptible to quantitative reduction, but this conclusion does not apply to the nitrochloro compounds, so far as studied. *o*- and *p*-Nitrochlorobenzene, for example, were reduced to the extent of only 70 to 80 per cent. When the chlorine is present in a side chain, on the other hand, it seems to have but little effect, as illustrated in the case of *p*-nitrobenzyl chloride. The presence of other strongly negative groups in addition to the chlorine, however, invariably resulted in over-reduction, probably at the expense of the chlorine atom. Examples of this over-reduction are to be found in the cases of dinitrochlorobenzene and the dihydrate of *p*-nitrochlorobenzene-*o*-sulfonic acid (1-chloro-2-sulfonic-4-nitro).

TABLE IV—PERCENTAGE REDUCTION OBTAINED FOR VARIOUS NITROCHLORO DERIVATIVES OF BENZENE

o-Nitrochlorobenzene M. P. 32.5°	*p*-Nitrochlorobenzene M. P. 83.0°	*p*-Nitrobenzyl chloride M. P. 72.57°	Dinitrochlorobenzene M. P. 49.8°	Nitrochlorobenzene Sulfonic Acid
77.5	74.0	100.5	102.1	100.5
67.2	81.4	100.3	102.2	100.6
66.8	68.3	100.7	105.3	100.5
....	71.4	100.4	101.5	100.4

DINITRO COMPOUNDS—The study of the dinitro compounds has so far not been very extensive, but the results indicate that the method is generally applicable with at least sufficient accuracy for control analyses.

TABLE V—PERCENTAGE PURITIES OBTAINED FOR VARIOUS DINITROBENZENE DERIVATIVES

m-Dinitrobenzene M. P. 84 4°	1,2,4-Dinitrotoluene M. P. 70.1°	Picramic Acid M. P. 169.9°
100.11	99.93	99.92
100.00	99.99	100.02
100.14	100.05	......
99.99	99.85	......

The method has also been successfully applied to dinitroxylyl dichlorides [$C_6H_2.(CH_2Cl)_2.(NO_2)_2$], thoroughly satisfactory results having been obtained upon the pure 1,3-CH_2Cl-2,4-NO_2 compound, as well as upon the mixtures of isomers resulting from commercial nitrations.

TRINITRO COMPOUNDS—All of the trinitro compounds investigated were found to be easily and quantitatively reducible. The following results upon trinitrotoluene and picric acid indicate the accuracy that may be expected in the analysis of this class of compounds.

TABLE VI—PERCENTAGE PURITIES OBTAINED UPON TRINITROBENZENE DERIVATIVES

Trinitrotoluene M. P. 80.78°	Picric Acid M. P. 122.5°
99.94	100.14
99.90	100.16
99.87	100.17
99.96	100.15

Other trinitro compounds successfully analyzed were trinitroxylene and trinitroaniline. It will be noted that the results given above for picric acid are about 0.15 per cent high. They have been checked by several analysts working independently upon samples purified in different ways, but in all cases results between 0.1 and 0.2 per cent high were obtained. It is interesting to note that the purities found by Knecht and Hibbert[1] are almost identical with the above.

TETRANITRO COMPOUNDS—Tetryl (*sym*-trinitrophenylmethylnitramine) was the only representative of this class considered. Complete reduction could not be obtained by the regular procedure with a 0.05 *N* solution of $TiCl_3$, and the analysis was not considered sufficiently important to warrant investigation. The few results obtained indicated that three of the nitro groups were completely reduced and the fourth partially. It is reasonable to suppose that the nitro group attached to the side chain is the refractory one.

NAPHTHALENE DERIVATIVES—Although very little work has been done upon the nitro naphthalene derivatives, preliminary experiments seem to indicate, as in the benzene series, that the presence of other substituents in general facilitates the reduction. Thus, α-nitronaphthalene is reduced to the extent of only 60 to 70 per cent by the standard procedure, while promising results were obtained upon two of the dinitrodisulfonic acid isomers.

CONCLUSIONS

The results obtained upon the various classes of nitrobenzene derivatives seem to justify the following general conclusions:

1—Mononitro hydrocarbons are exceedingly resistant toward reduction by titanous chloride.

2—The presence of positive or negative substituents, with the exception of chlorine, in the nucleus facilitates the reduction of the nitro groups.

3—It would appear, further, that the orientation of the substituents with respect to the nitro group has no appreciable effect; thus, *m*- and *p*-nitroaniline are reduced with equal ease, as are *o*- and *p*-nitrophenols, *o*- and *m*-nitro-*p*-toluidines, and two of the nitrosalicylic acid isomers. Conversely, *o*- and *p*-nitrochlorobenzenes are about equally refractory.

Since the completion of the work described above, the results of an investigation conducted by Callan, Henderson and Strafford[2] along similar lines have been published.

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[1] These two compounds, as well as the *o*-nitrophenol, were synthesized and analyzed by W. L. Perdue of this laboratory.

[1] *Loc. cit.*, **1918**, p. 27.

[2] *J. Soc. Chem. Ind.*, **39** (1920), 86*t*.

THE ANALYSIS OF MOLYBDENUM, COBALT, AND CHROMIUM ALLOYS

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In recent years certain alloys of molybdenum, cobalt, and chromium have assumed commercial importance. Stellite, which makes remarkable cutting tools, has been found by the French government[1] to have twice the cutting power of the hardest carbon steel. In a study of this alloy no difficulty was found in preparing metal somewhat similar to stellite, but trouble was experienced in making the analysis. According to Peele,[2] stellite consists of 10 to 25 per cent chromium, 75 to 90 per cent cobalt, with traces of molybdenum and tungsten. Johnson,[3] however, gives its composition as: cobalt 60.80 per cent, molybdenum 24.10 per cent, chromium 13.20 per cent, with small amounts of iron, manganese, silicon, and phosphorus. Since the alloy is said to be prepared in the carbon arc furnace, a complete analysis should include a determination of carbon.

The alloys to be analyzed were prepared on a small scale by the aluminothermic reduction of the oxides, using for preliminary trials 41.39 g. Co_2O_4, 18.07 g. MoO_2, and 9.7 g. Cr_2O_3, mixed with 22.6 g. aluminium, and about 10 g. calcium fluoride to slow up the reaction. It was afterward shown that these first samples were not very similar in composition to stellite, as claimed by either Peele or Johnson. Attempts were made to analyze this alloy by the method given by Johnson. The following table shows that incomplete separations were made on two different samples, some of the molybdenum separating with the cobalt and some of the cobalt with the molybdenum, making the total percentage considerably over 100.

Element	Sample I	Sample II
Cobalt	87.70	81.84
Molybdenum	29 56	51.40
Chromium	0.82	0.03
Total	118.08	133.27

In view of this difficulty the various methods of precipitation and determination of these metals were tried out. The following table shows some of the results obtained on Sample 1:

Method	Cobalt Per cent	Molybdenum Per cent	Chromium Per cent
Johnson[1]	87.7	29.56	0.82
Scott[2]	...	23.95	..
Smith[3]	81.06	21.69	..

[1] *Loc. cit.*

[2] "Standard Methods of Chemical Analysis," D. Van Nostrand Co., N. Y., **1917**.

[3] "Electro-Analysis," Blakiston & Sons, Philadelphia, **1911**.

Trials of other methods, such as the determination of cobalt by the potassium cobaltinitrate method and the titration of molybdenum with lead acetate using tannic acid as an indicator,[4] were not attended with success.

The best results were obtained by the following method: Place the sample in a 200 cc. Erlenmeyer flask and add a few cc. each of concentrated hydrochloric and nitric acids. (The weight of sample taken depends on the composition of the alloy. Both the peroxide and sulfide separations work best when the quantities of metal are small.) Heat gently or allow to stand over night until the alloy is all dissolved, cool, add 3 cc. concentrated H_2SO_4, and evaporate, until white fumes just begin to appear, to remove the excess of aqua regia. Cool, dilute to 100 cc., and transfer to a small pressure bottle. The solution is of the proper acidity for the preparation of molybdenum. Pass hydrogen sulfide into the solution for 5 to 10 min. to thoroughly saturate, close the bottle and place it in boiling water. After boiling for one hour, allow to cool and let the precipitate settle. Filter, wash with cold water until the washings show no acidity to litmus, and again saturate the filtrate with hydrogen sulfide and boil to insure complete separation of the molybdenum. It is usually advisable to redissolve and reprecipitate the MoS_2 in order to make the separation complete. Ignite the precipitate of MoS_2 at a dull red heat in the muffle for 2 hrs. and weigh as MoO_3.

Boil the filtrate to remove hydrogen sulfide, cool, and add sodium peroxide to precipitate completely the cobalt, as $Co(OH)_3$. Boil, filter, and wash with dilute hydrogen peroxide until the precipitate is free as possible of sodium hydroxide. In most cases it is necessary to redissolve the precipitate in 1:1 hydrochloric acid and peroxide again to insure a complete separation. Ash the black cobaltic hydroxide, and weigh as Co_3O_4.

Acidify the filtrate from the peroxide treatment with sulfuric acid, and boil to free the solution from hydrogen peroxide. Titrate the chromates in the solution with ferrous ammonium sulfate solution, using either electromotive force measurements in the solution or potassium ferricyanide as an outside indicator. Most excellent results may be obtained using the electromotive force titrations, but they take more time than the better-known spot plate method and were used in this work only for standardizations.

In tests upon solutions of known composition the percentages of cobalt, molybdenum, and chromium checked within the limits of experimental error. The following table shows the results of a series of analyses made on samples of metal obtained by the aluminothermic reduction of a mixture of 20 g. each of Co_3O_4, Cr_2O_3, MoO_3, and Al powder.

Sample No.	1	2	3	4	5	Average
Molybdenum	41.40	41.05	41.07	42.27	(41.79)	41.52
Cobalt	50 30	51.63	(50.89)	50.66	51.00	50.89
Chromium	7.63	7.69	7.59	7.16	7.75	7.56
Total						99.97

A RAPID AND SYSTEMATIC METHOD FOR THE ANALYSIS OF LIGHT ALUMINIUM CASTING ALLOYS

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Since alloys containing 90 or more per cent of aluminium are practically insoluble in nitric acid, the usual procedure for analysis has been to dissolve the alloy in aqua regia, fume out the hydrochloric acid with sulfuric acid, and proceed in much the same way as with other alloys.

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[1] *Iron Age*, May 10, 1917.

[2] "Mining Engineers' Handbook," John Wiley & Sons, Inc., N. Y., **1918**.

[3] "Rapid Methods for Chemical Analysis of Special Steels," John Wiley & Sons, Inc., N. Y., **1914**.

[4] *Mining Sci. Press*, **1916**, 113.

Inasmuch as time, as well as accuracy, is a large factor in most laboratories, the above method is objectionable because it is slow and tedious, and unless extreme care is taken considerable error will be introduced by the occlusion of other metals in the aluminium hydroxide. Also, the amount of acid which must be present to keep the aluminium in solution during electrolysis makes it difficult to remove the last traces of copper.

In the following procedure the loss of time due to fuming out the hydrochloric acid and concentration of filtrates is eliminated. The accuracy of the method lies in the fact that a larger sample may be taken for analysis, inasmuch as the main bulk of the aluminium is removed at the start from all the other metals, except the zinc, thereby making it much easier to handle the remaining elements.

METHOD OF PROCEDURE

Dissolve one gram of the alloy in 20 cc. of a 25 per cent sodium hydroxide solution, and dilute to 300 cc. immediately after effervescence ceases. The dilution must be made at once because, although tin is practically insoluble in dilute solutions of fixed alkali at normal temperatures, it does dissolve slowly in concentrated solutions at high temperatures.

Filter through a No. 41 Whatman filter and wash at least 10 times with one per cent sodium hydroxide. The alkali-insoluble portion contains the tin, copper, lead, iron, nickel, and magnesium, part of the manganese, and traces of aluminium. The filtrate will contain about 99 per cent of the aluminium and zinc, and the remainder of the manganese.

ANALYSIS OF THE FILTRATE

To the filtrate, add formic acid (sp. gr. 1.2) until the solution is just acid to litmus paper, then add 25 cc. of formic acid in excess. (The solution will be cloudy, but will clear on boiling.) Heat to boiling and pass a rapid stream of H_2S into the liquid for 30 min. If zinc is present the white sulfide will be observed adhering closely to the end of the delivery tube and to the beaker, at the surface of the liquid. Filter on a 15 cm. No. 42 Whatman filter paper, and wash with hot water. Return paper and precipitate to the original beaker and digest on a steam bath with 20 cc. of 1 : 1 HCl for 30 min. Filter, and wash with hot water. Boil the filtrate and washings until all hydrogen sulfide is removed, and titrate with potassium ferrocyanide according to the method given by Heath.[1]

ALKALI-INSOLUBLE PORTION

TIN—Transfer the filter paper containing the original alkali-insoluble portion to a 250 cc. beaker and add 10 cc. of concentrated nitric acid. Cover with a watch glass, and digest on a hot plate until everything soluble goes into solution, and the tin is converted into metastannic acid. Dilute with 20 cc. hot water and digest 10 min. longer. Filter through a double filter of No. 44 Whatman filters. Wash 5 or 6 times with hot water. Extract the paper with the tin precipitate in a small beaker or flask by heating gently with 20 cc. of yellow ammonium sulfide and 2 g. of ammonium chloride, filter, and wash thoroughly with dilute yellow ammonium sulfide. This dissolves the tin, while silica and any black sulfides of copper, lead, or iron are filtered off. The polysulfide solution, after filtering, is made acid with 50 per cent acetic acid, heated to boiling, again filtered, and the precipitate of tin sulfide is washed with ammonium acetate solution saturated with hydrogen sulfide. The tin sulfide is ignited directly with the moist paper to SnO_2, care being taken to ignite to constant weight. This ignition must proceed slowly and carefully until the sulfur is roasted off. If the sulfur is allowed to burn, some tin sulfate may be formed. If the SnO_2 weighs more than 20 mg., the blast lamp should be used.

$$\frac{\text{Wt. of } \mathrm{SnO_2} \times 78.77}{\text{Wt. of sample}} = \text{Per cent Sn}$$

COPPER AND LEAD—The first filtrate from the tin is caught in a 200 cc. electrolytic beaker, diluted to 150 cc. with distilled water, and electrolyzed for copper and lead with a current of one ampere and 2.5 volts. After one-half to three-quarters of an hour, the sides of the beaker and cover glasses are washed down with enough distilled water to raise the surface of the solution about 0.25 inch. If after 10 min. no black deposit collects on the newly exposed portions of the anode, all lead has been removed from the solution. Two cc. of 1 : 1 sulfuric acid are now added to bring the electrolyte back to its original acid concentration and to allow the last trace of copper to plate out. When all the copper has apparently been removed, dilute with the same amount of water as before and continue the current. If at the end of 10 min. no deposit shows on the newly exposed part of the cathode, all copper has been removed. Cathode and anode are at once removed from the electrolyte, washed twice with distilled water, and once with alcohol. The cathode is dried in an oven at 80° C. for 15 min., and the anode in a separate oven at 210° C. for 0.5 hr. The increase in weight of the cathode is the copper in the sample, while the increase in weight of the anode is PbO_2.

$$\frac{\text{Wt. of Cu} \times 100}{\text{Wt. of sample}} = \text{Per cent Cu}$$

$$\frac{\text{Wt. of } \mathrm{PbO_2} \times 86.62}{\text{Wt. of sample}} = \text{Per cent Pb}$$

IRON—To the electrolyte from the copper and lead determination, add 2 or 3 g. of ammonium chloride, and make barely ammoniacal with ammonia. Boil off any excess ammonia, allow to settle, and filter off the iron and traces of aluminium.[1] Wash well with distilled water, redissolve the iron and aluminium hydroxides in dilute hydrochloric acid, and titrate the iron with potassium permanganate, after reduction with stannous chloride. (Zimmerman-Reinhardt Method.)

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[1] "Analysis of Copper," 1st Ed., **1916**, p. 249, or Price and Meade, 2nd Ed., **1917**, p. 165.

[1] It is the experience of the writer that whatever manganese is precipitated with the Sn, Cu, Pb, Fe, Ni, and Mg in dissolving the alloy is so small that the ammonium chloride just added prevents more than traces of it for precipitating with the hydroxides of iron and aluminium, and therefore does not affect the titration of the iron

NICKEL—The filtrate from the iron and aluminium hydroxides is neutralized and made just acid to litmus with hydrochloric acid.[1] Heat nearly to boiling and add dimethylglyoxime, make just ammoniacal, and place on a low heat hot plate for an hour. Filter through a weighed Gooch crucible, wash well with hot water and finally with alcohol. Dry in an oven at 110°, and weigh.

$$\frac{\text{Ni ppt.} \times 20.31}{\text{Wt. of sample}} = \text{Per cent Ni}$$

MAGNESIUM—Make the filtrate from the nickel precipitation strongly ammoniacal and heat to boiling, and precipitate the magnesium with ammonium phosphate. Cool in a sink of cold water for 4 or 5 hrs. and filter off the ammonium magnesium phosphate through a Gooch crucible, previously *ignited* to constant weight. Wash well with 2 per cent ammonia solution and ignite to constant weight in a high-temperature muffle furnace, or with full heat of the blast lamp. Weigh as $Mg_2P_2O_7$.

$$\frac{Mg_2P_2O_7 \times 21.839}{\text{Wt. of sample}} = \text{Per cent Mg}$$

MANGANESE—Treat one gram of the alloy with 25 per cent sodium hydroxide solution, add sufficient concentrated nitric acid to dissolve the alkali-insoluble matter, followed by 30 per cent excess acid. Add a few crystals of silver nitrate, boil, and oxidize with ammonium persulfate. Cool and titrate rapidly with standard arsenite solution, as described by Johnson.[1]

SILICON—Dissolve one gram of alloy in 10 cc. of a mixture of nitric and sulfuric acids and water (450 cc. HNO_3: 250 cc. H_2SO_4: 1000 cc. H_2O) with a few drops of concentrated hydrochloric acid added. Evaporate to complete dryness. Take up with 50 cc. concentrated hydrochloric acid and hot water. Heat to boiling, filter, ignite, and weigh. Treat the ash with hydrofluoric acid, and determine the loss in weight.

$$\frac{\text{Loss in wt.} \times 46.93}{\text{Wt. of sample}} = \text{Per cent Si}$$

CONCLUSION

By the above method it is possible to make a complete analysis of a sample of aluminium alloy in the time usually spent in fuming out hydrochloric acid and concentrating filtrates. Moreover, more accurate results are easily obtained.

The following percentages were obtained by the writer upon three samples of alloy analyzed by the new method:

	Sample A		Sample B		Sample C	
Mn	0.01	0.01	...	...	0.02	0.02
Si	0.33	0.33	0.47	0.46	0.02	0.01
Zn	...	...	...	...	0.55	0.55
Sn	1.55	1.62	0.20	0.26	...	...
Cu	7.71	7.70	7.65	7.60	2.43	2.43
Pb	0.05	0.05	0.05	0.05	...	...
Fe	0.12	0.13	0.30	0.32	0.21	0.26
Ni	0.28	0.21	0.27	0.23	1.19	1.19
Mg	0.10	0.12	0.20	0.19	1.04	1.04
Al	89.85	89.83	90.86	90.89	94.55	94.50

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[1] If the nickel is precipitated in a *very slightly acid* solution, which is then made just ammoniacal, it comes down in a more crystalline form, which is easier to filter and wash.

[1] "Chemical Analysis of Special Steels, Steel-Making Alloys and Graphites," 2nd Ed., **1914**, p. 283.

LABORATORY AND PLANT

SODA LIME AS AN ABSORBENT FOR INDUSTRIAL PURPOSES[1,2]

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Although soda lime has long been a familiar reagent in the laboratory, and has frequently been used for absorbing various acid gases on a fairly large scale, the literature contains practically nothing concerning the best methods for its preparation. A few of the older reference books state that it is made by "stirring lime into molten caustic to cook, and breaking up the resultant cake." This seems to be essentially the standard commercial process of to-day. As will be indicated later by comparative tests, soda lime made by any such process has many undesirable physical properties, and its efficiency in gas absorption is extremely low.

As has been previously pointed out by the writer and others,[3] soda lime was one of the main constituents of the absorbent mixture used in all American gas-mask canisters for the absorption of toxic gases. On account of its importance from a defensive standpoint, an extremely careful study was made of every factor which might possibly have a bearing on the stability or absorptive efficiency of the product under any conceivable service conditions. Experiments were carried out both on a small and a large scale until the effect of practically every variable in the raw materials or the method of preparation was thoroughly appreciated.

REQUIREMENTS FOR MILITARY SODA LIME

The soda lime which was devised for military purposes had to meet four rather exceptional requirements which placed severe limitations on its composition and resulting absorptive activity. In the first place, it had to possess a high degree of hardness or resistance to abrasion, on account of the extremely severe handling to which the canisters were subjected during transportation over rough roads in motor trucks, and during actual service in the trenches. In order to secure this degree of hardness it was necessary to use a considerable amount of binding agent in the soda lime, which greatly reduced its absorptive activity.

A second requirement was that it must not be sufficiently hygroscopic to form any free solution or tend to cake together even after prolonged use in very moist air. This requirement completely eliminated the ordinary types of soda lime containing from 20 to 40 per cent sodium hydroxide.

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[1] Published by permission of Brig. Gen. Amos A. Fries, Chief, C. W. S., U. S. Army.

[2] Presented at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

[3] This Journal, **11** (1919), 420.

It also seemed desirable to have in the soda lime some active oxidizing agent which would remain stable over long periods of time when not exposed to gas. Pure sodium permanganate in the presence of a *small* amount of alkali proved best for this purpose. This imposed very definite limitations on the alkali content of the soda lime.

In the fourth place, absorptive *capacity* was relatively more important for military purposes than absorptive *activity* (the rate of taking up the gases), because in general the concentrations of gas in the field were very low, but persistent over long periods of time, and the difficulty and cost of supplying new canisters were great.

REQUIREMENTS FOR INDUSTRIAL SODA LIMES

For industrial purposes the conditions which must be met are greatly different. In the first place, the concentrations to be encountered are higher, which places a premium on absorptive activity, while the ease of replacing the canisters is much greater, so that absorptive capacity could be sacrificed if necessary. Second, in industrial uses the canister will in general receive very little rough handling, certainly not a tenth as severe as that to which the military canister was subjected. Finally, there is in general no need of providing an oxidizing agent to handle a few special gases which would probably never be encountered in industrial work.

In order to devise a soda lime which would be really well adapted for industrial purposes, it was necessary to re-survey the whole field, striking a new balance between the various desirable properties and aiming in this case to get the maximum absorptive activity, coupled with a reasonable, but not high, degree of hardness or resistance to abrasion.

Shortly before the signing of the armistice the Research Division, Chemical Warfare Service, undertook an intensive study of absorbents for industrial purposes. This was not entirely completed before the cessation of experimental work at the American University, but has now been completed in this laboratory.

EXPERIMENTAL METHODS

Although the objects of this work were somewhat different from that previously undertaken, the experimental methods which had already been worked out were of great advantage in getting rapid and accurate results. The general steps in the process of manufacture had so clearly demonstrated their worth for a wide variety of formulas that it was decided to adopt them, at least as a preliminary basis for the experimental work. The steps in the manufacture (see previous article for details) consisted essentially in mixing the dry ingredients thoroughly with a solution of caustic soda, adding just enough water to make possible thorough and uniform mixing without any tendency toward fluidity. The maintenance of this stiff consistency was found to be very important in getting satisfactory hardness in the finished granules. The plastic mass was then spread by hand on wire-bottomed trays into slabs, which were allowed to set for about 3 days in a room of approximately normal temperature and humidity, during which time the soda lime lost about 10 per cent of its moisture. It was then dried under carefully controlled conditions for about 12 hrs., ground, and screened to the desired mesh (usually 8 to 14). Each of the foregoing details was found of definite importance in securing a maximum degree of hardness, coupled with the degree of porosity necessary to give high absorptive activity.

Of the greatest assistance in carrying out this investigation was the presence of a trained corps of men who were thoroughly experienced and appreciated the importance of controlling every detail in the process of manufacture, if dependable and reproducible results were to be secured. Another important factor was the routine testing methods which had been very carefully worked out and standardized to show the efficiency of absorbents against a wide variety of gases.

As a result of this previous experience it was possible in the experiments hereinafter described to obtain a remarkable concordance between check results. In fact, most of the results were reproducible within 5 per cent, as compared with variations of 50 to 100 per cent which very frequently occurred during the earlier work. Those who have had experience in preparing synthetic granular materials of high porosity for catalytic or absorbent purposes will bear witness to the fact that concordant and reproducible results are extremely difficult to obtain except under the very best conditions.

At the outset it seemed desirable to study mixtures containing only alkali and lime, omitting the kieselguhr and cement which were used in the army formula to give hardness, and the sodium permanganate which was used as an oxidizing agent. Such simple mixtures had, of course, been previously tested out in a preliminary way, but found unsatisfactory for military purposes on account of their lack of hardness, although their great absorptive activity was recognized.

SELECTION OF LIME—The first experiments were designed to determine the best brand of lime. A dozen lots of hydrated lime from different sources were made up into a standard preliminary formula containing 4 per cent sodium hydroxide and 96 per cent calcium hydroxide. These samples showed a wide variation in absorptive efficiency, the average service time against gases being about 60 per cent of the maximum, while the minimum fell as low as 20 per cent of the maximum. The hardness of the granules was also quite variable.

While the results were reproducible and conclusive as far as the selection of the best brand was concerned, it was not found possible to coördinate them with the chemical analyses of the various samples of lime. Certain general conclusions, however, may be stated as follows:

(1) Hardness was in general inversely proportional to absorptive efficiency. This was apparently caused by the formation of sodium silicate during the drying, due to a reaction between the alkali and the silica present in the lime. The harder samples invariably gave a precipitate of silicic acid when dissolved in acid. This sodium silicate served as a binding agent, but also tended to clog up the pores of the absorbent.

(2) The tendency to form sodium silicate was not directly proportional to the amount of silica present in the lime. There is apparently a great difference in the reactivity of the silica present in different samples of lime, which may be due either to fineness of subdivision or possibly to its existence as calcium or magnesium silicate in some cases, and as free silica in others.

(3) Limes containing over 5 per cent of magnesium oxide did not give as good results as the high calcium limes. Even fairly high dolomitic limes, however, gave absorptive efficiencies as high as 70 per cent of the maximum.

(4) A low content of CO_2 and Fe_2O_3 seemed to be desirable.

(5) Extra fine, air-separated lime gave granules which were harder, but not as absorptive, as those made with lime of normal fineness (about 90 per cent through 200 mesh).

(6) Completeness of hydration seemed to be important to insure stability and hardness of the resulting granules. The evidence on this point is, however, rather indirect, as the analytical results for combined water were found to be variable and unsatisfactory, as might be expected, and the Bureau of Standards "soundness test," designed to show completeness of hydration, did not parallel the results obtained on soda lime. The evidence as to the effect of completeness of hydration is that certain samples, which showed a distinct tendency to crumble on standing in moist air for several days after manufacture, lost this tendency when the original lime was rotated in a ball mill with water for several days.

On the basis of the foregoing tests, two brands of lime stood out as giving very good absorptive activity and apparently adequate hardness. As the results obtained with the two samples were not greatly different, one brand was arbitrarily selected for most of the tests, while a few comparative batches were later made with the other brand.

AMOUNT OF ALKALI AND WATER—Having determined the best brands of lime, and the method of manufacture which appeared to give maximum hardness, there remained the two fundamental variables—the NaOH and H_2O contents of the soda lime—which were the main objects of this study.

Several different types of gas were selected as tests of the value of the soda lime for general industrial purposes. Phosgene ($COCl_2$) was selected as a gas which must be hydrolyzed to be absorbed, and which then acts as a strong acid gas. The test was run at a fairly high concentration (one per cent by volume), and had been found a severe test of the *activity* of the absorbent. Superpalite ($CCl_3.COOCl$), which behaves similarly to phosgene, was run at a much lower concentration to test absorptive capacity rather than activity. Sulfur dioxide was used as an example of an acid gas of medium strength, and carbon dioxide as a very weak acid gas, but one whose quantitative absorption is extremely important in many analytical processes. Chlorine was selected as a gas of still different type of considerable industrial importance. An absorbent which would give good results against these five gases could certainly be relied upon for general industrial purposes, especially if mixed with charcoal.

In studying two independent variables, it is customary to hold one constant while the other is varied. This is difficult in the case of soda lime, however, because it is very hard to approximate the desired final water content after drying down, grinding, and screening small samples; yet in many cases the water content is more important than the alkali content. Furthermore, if a systematic attempt is made to cover the whole field in this way, the number of experiments required is very large.

A somewhat more convenient method of obtaining the same result, and one which could well be used more frequently where one of two variables is hard to control but easy to determine, is to vary both factors simultaneously as they happen to occur, and to represent the results, theoretically in three dimensions, but practically by locating the points on a plane surface (in this case with the NaOH and H_2O contents as coordinates), designating the efficiency (service time) by numerical figures corresponding to each point, and drawing in contour lines to represent horizontal sections of equal efficiency in the hypothetical three dimensional diagram. These contours serve to show very clearly the optimum combination of the two variables to give the maximum service time against each gas, and by passing sections through, parallel to either axis, it is easy to determine the effect of either variable when the other is held constant. When the results of the first series of ten or twelve experiments are plotted in this way it is a simple matter to determine the especially interesting or doubtful portions of the field, and to fill in the vacancies by a very few more experiments.

The tabulated results of the principal series of experiments are shown in Table 1. They do not include the results against CO_2, which were determined previously upon another series of similar composition, but mostly with higher water content. The latter work was carried out with a specific purpose in view, which accounts for the fact that the test conditions are considerably different from those used for the other four gases.

TABLE 1—DATA ON "H" SERIES SODA LIME

				Service Time to 99 Per cent			
NUMBER	NaOH Per cent	H_2O Per cent	Hardness	Cl_2	Superpalite	Phosgene	SO_2
H204......	1	6.78	58.2	32	215	31	34
H205......	2	7.76	69.4	40	213	31	43
H206......	3	9.64	63.0	44	224	31	52
H207......	4	10.42	80.0	65	237	31	58
H208......	5	15.20	87.8	62	185	27	60
H209......	6	8.34	96.0	57	189	30	46
H210......	8	12.98	82.0	25(?)	145	34	65
H211......	10	6.43	78.0	72	180	29	41
H212......	12	12.94	82.0	83	124	27	51
H213......	15	8.10	76.2	100	172	27	27
H214......	5	11.22	84.4	60	200	34	56
H215......	1	9.87	37.4	36	207	30	44
H216......	2	13.44	57.4	29	207	38	61
H217......	4	13.18	..	45	207	38	68
H218......	4	4.56	86.1	37	202	28	33
H220......	4	7.97	37.6	51	228	33	43
H221......	4	11.22	41.2(?)	..	242	35	59
H222......	8	16.34	84.3	55	122	25	55
H243......	5	19.80	90.6	27	134	22	46
H244	2.5	12.60	81.8	31	212	37	66

DISCUSSION OF RESULTS—In order to appreciate the significance of the results, reference should be made to the five plates on which the service times for each point are indicated numerically, and contour lines of equal service time are drawn.

Sulfur Dioxide—Plate I, showing the SO_2 efficiency for the different samples, illustrates very clearly the method of constructing the plots. Here a very marked maximum service time occurs at about 5 per cent alkali and 13 per cent water, any considerable variation from this point giving poorer results.

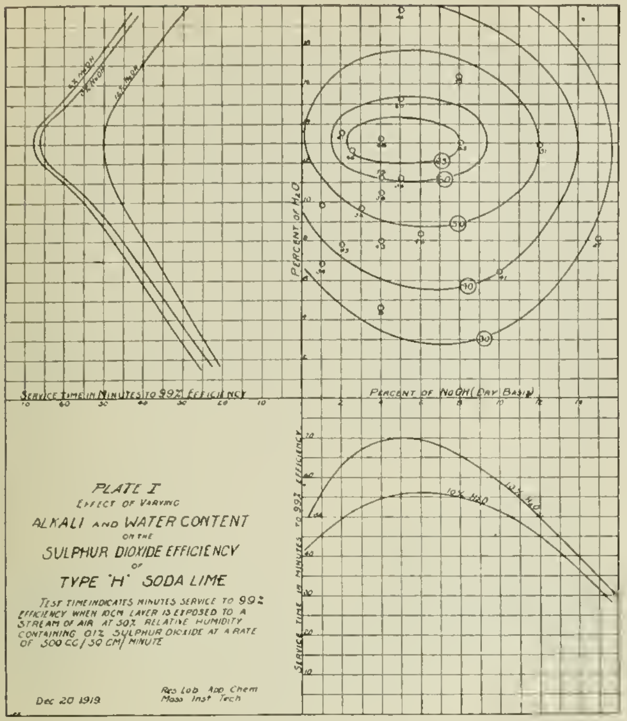

PLATE I
EFFECT OF VARYING
ALKALI AND WATER CONTENT
ON THE
SULPHUR DIOXIDE EFFICIENCY
OF
TYPE "H" SODA LIME

TEST TIME INDICATES MINUTES SERVICE TO 99% EFFICIENCY WHEN 10 CM LAYER IS EXPOSED TO A STREAM OF AIR AT 50% RELATIVE HUMIDITY CONTAINING 0.1% SULPHUR DIOXIDE AT A RATE OF 500 CC/50 CM/MINUTE

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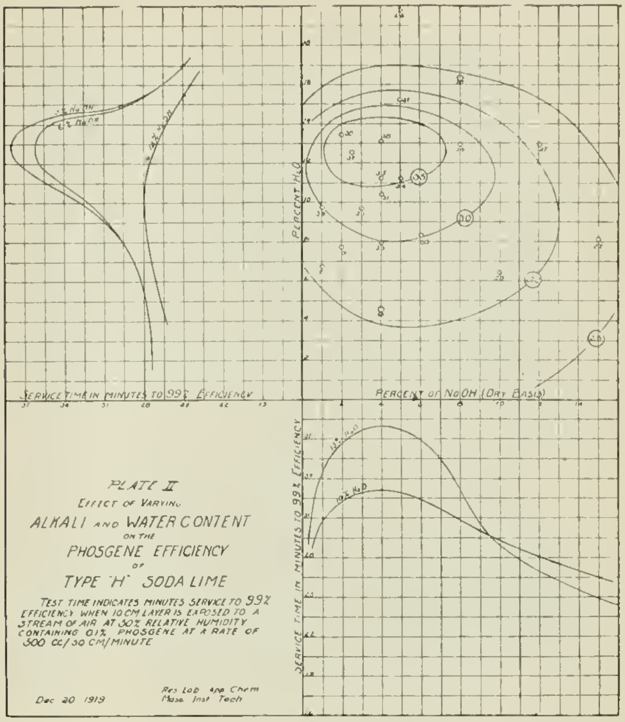

PLATE II
EFFECT OF VARYING
ALKALI AND WATER CONTENT
ON THE
PHOSGENE EFFICIENCY
OF
TYPE "H" SODA LIME

TEST TIME INDICATES MINUTES SERVICE TO 99% EFFICIENCY WHEN 10 CM LAYER IS EXPOSED TO A STREAM OF AIR AT 50% RELATIVE HUMIDITY CONTAINING 0.1% PHOSGENE AT A RATE OF 500 CC/50 CM/MINUTE

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Inspection shows that the results are all remarkably consistent and that the contour lines as drawn represent very closely the service times which can be expected for any combination of the two fundamental variables. It is true that the exact location of the curves in the upper part of the figure is not especially definite, but the curves are drawn in on the assumption that they are reasonably smooth and continuous between known points. They are certainly well established in the immediate vicinity of the maximum, which is the important part of the field.

The contours of equal service time are obviously elliptical in shape near the maximum, with the long axis on the 13 per cent H_2O line. This indicates that in this vicinity the water content is a more important variable than the alkali content.

By passing sections through the contours parallel to the two axes it is possible to determine fairly accurately the effect of varying the NaOH content with the H_2O content constant, or *vice versa*. The curves thus obtained are shown in the two sections of the figure adjoining the contour curves. It will be noted, for example, that 13 per cent H_2O gives the maximum service time regardless of the amount of NaOH present.

Phosgene—Plate II, for phosgene, gives very similar results, with a maximum at practically the same point. In this case, however, the maximum is by no means so sharply defined—for example, decreasing the water content to 4 per cent cuts the SO_2 service time to 50 per cent of the maximum value, while the $COCl_2$ service time at this point is still 73 per cent of the maximum.

Carbon Dioxide—Plate III, which presents the results on the very weakly acid gas CO_2, shows a very pronounced maximum—in this case at about 4.5 per cent alkali and 18 per cent H_2O. The high water content required to give the best results is at variance with the results on all other gases, but seems to be well established. Here again the results for water contents above 18 per cent are very uncertain, and there is really little justification for prolonging the contours in this region. This part of the field has little interest, however, since it is impractical to work with such high water contents, and the maximum is unquestionably approximately as indicated.

Superpalite—The results shown in Plate IV for superpalite appear at first sight to be quite at variance with the results on Plate II for the very similar gas, phosgene. The variation is due, however, to the difference in the conditions of test—the superpalite test being run at a much lower concentration, and lasting for a longer time. As a result, the initial water content is of much less importance in the neighborhood of the maximum, since this adjusts itself by taking up or giving off moisture to the 50 per cent humid air which is passing through the tube during the test. If the results were plotted against *final*, rather than *initial*, water contents, the curves would probably be very similar for the two gases. For the higher NaOH soda limes, however, a sample which would start with about 12 per cent water would pick up possibly 6 per cent more before the end of the test, while very dry samples—containing, say, 4 or 5 per cent water—would approach the optimum water content at about the end of the test. Samples containing much alkali, therefore, would be expected to give the best results when they had very little water to start with, as is actually indicated by the contours.

Chlorine—Plate V shows the very different type of contours which are obtained with chlorine, which appears to be absorbed in a somewhat exceptional manner. Here the water content is relatively unimportant, while

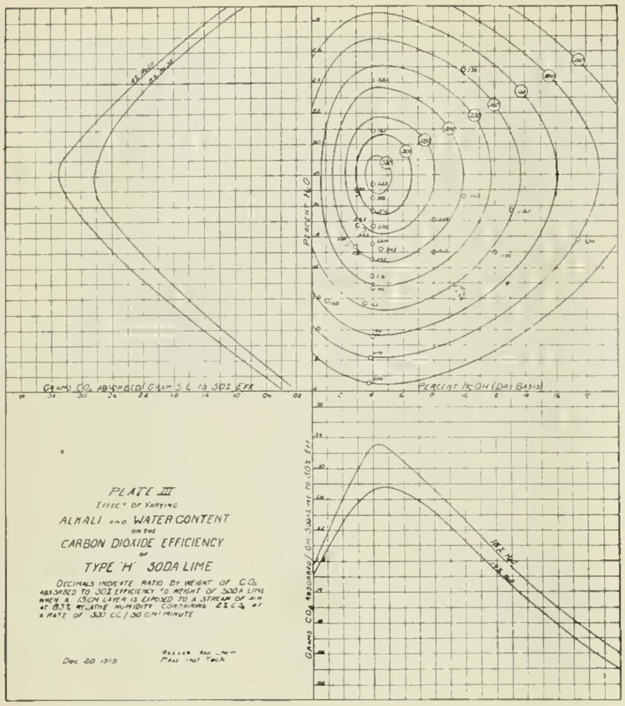

PLATE III
Effect of Varying
ALKALI AND WATER CONTENT
ON THE
CARBON DIOXIDE EFFICIENCY
OF
TYPE "H" SODA LIME

Decimals indicate ratio by weight of CO₂ absorbed to 50% efficiency to weight of soda lime when a 15 cm layer is exposed to a stream of air at 85% relative humidity containing 2% CO₂ at a rate of 500 cc/50 cm²/minute

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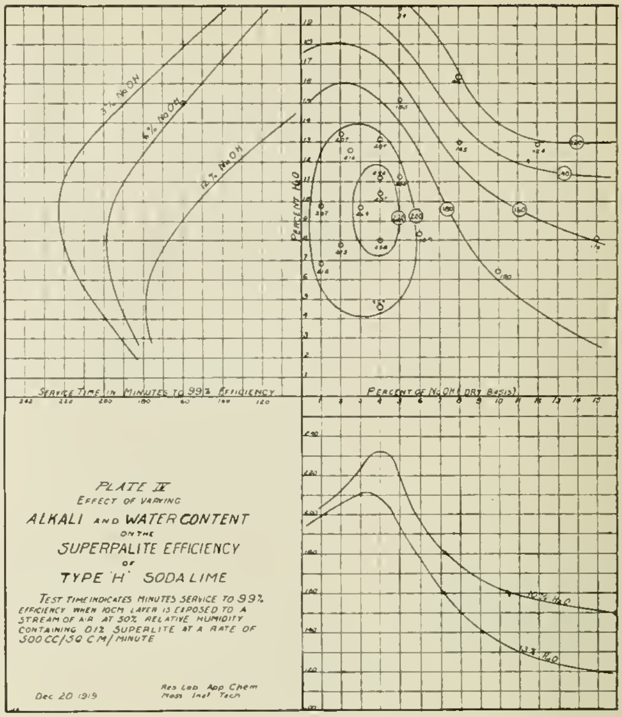

PLATE IV
Effect of Varying
ALKALI AND WATER CONTENT
ON THE
SUPERPALITE EFFICIENCY
OF
TYPE "H" SODA LIME

Test time indicates minutes service to 99% efficiency when 10 cm layer is exposed to a stream of air at 50% relative humidity containing 0.1% superalite at a rate of 500 cc/50 cm/minute

Dec 20 1919
Res Lab App Chem
Mass Inst Tech

a high alkali content seems to be essential for good results. Very possibly the calcium hypochlorite formed is markedly less stable than the sodium salt at the comparatively high temperature produced in this high concentration test. Since samples containing over 10 per cent alkali tend to be markedly deliquescent in service, no attempt was made to reach the maximum service time, which appears to be above 16 per cent alkali content. The indications are that water contents in the neighborhood of 10 per cent give the best results, but this is not very definitely established by the results obtained thus far.

HARDNESS—The most important remaining variable is the hardness of the various granules. These were determined by a special type of test which consisted essentially in placing 50 g. of the 8 to 14 mesh soda lime, together with 30 three-eighths inch steel ball bearings, in the pan of a Rotap shaking machine, and running for 30 min. This rather severe test abraded the softer granules to a considerable extent. The percentage hardness represents the per cent of the material remaining on a 20 mesh screen at the end of the test. By carefully standardizing the shape of the pan bottoms and the method of screening before and after the test, it was possible to secure very reproducible and significant results.[1]

When the preliminary plot of the hardness data was made for the foregoing series of soda limes, it was found that the water content was of practically no importance. The hardness values (Plate VI) are, therefore, plotted directly against the alkali content, disregarding the water content. (The hardness values for very high water contents above 16 per cent are probably higher than they should be, on account of the tendency of the fine material produced in the test to ball together and remain on the 20 mesh screen, instead of going through as they should.) The results indicate fairly clearly that up to 5 per cent alkali content the hardness is greatly increased by the alkali. Beyond 6 per cent there seems to be a slight but fairly definite decrease.

SELECTION OF OPTIMUM COMPOSITION FOR VARIOUS PURPOSES

Having thus presented in detail the effect of the alkali and water content on the various important properties of soda lime, there remains but to select the best combination of the two variables for different industrial purposes.[1] For soda lime to be used in gas-mask canisters for general toxic gas absorption, an alkali content of 5 per cent (dry basis) and a water content of 10 to 13 per cent appear to be the most desirable. Where soda lime is to be used almost solely for CO_2 absorption, as in steel analyses and oxygen-helmet apparatus for mine rescue work, etc., an alkali content of 4.5 per cent and a water content of 16 to 19 per cent appear to be the best. If chlorine only is to be dealt with, an alkali content as high as 8 or 9 per cent might well be used; higher alkali contents would give still better results in case of short service times in very high concentrations, but in ordinary service an 8 per cent alkali soda lime will give as good results against chlorine alone as one containing 12 or 15 per cent alkali, and the latter would be almost certain to give trouble from caking.

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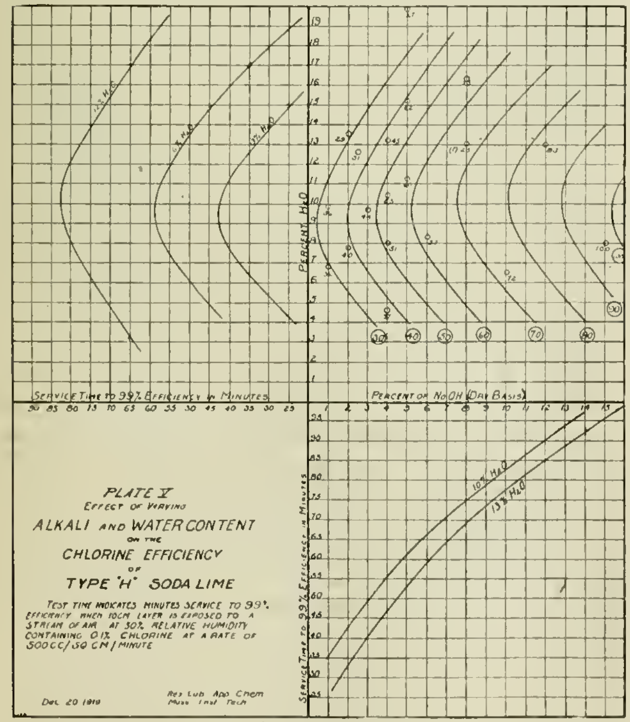
[1] By changing the length of time of the test and the number and size of the ball bearings it is possible to use this general method of testing hardness, and to secure a satisfactory degree of severity for practically any granular material. For example, the test was made much more severe for the regular army soda lime by using larger ball bearings (15.5 in. and 15³/₈ in.). It is believed that this method of testing should prove valuable for many different types of closely sized granular materials where hardness or resistance to abrasion is an important factor.

[1] The methods of manufacture and general formulas found best are covered by U. S. Patent 1,333,524.

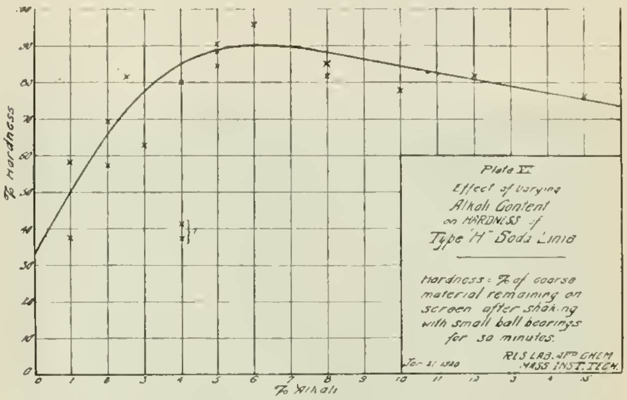
It must be again emphasized that the results presented in this report apply only to the specific method of manufacture previously described, and that within limits the method of manufacture is more important than variations in the formula. This seems to be especially true in the case of CO_2 absorption, where it is, of course, important to prevent exposure to air containing CO_2. Vacuum drying appeared to be slightly better than air drying for CO_2 absorption, but for other gases there appeared to be no difference. In the case of the CO_2 absorbent it is necessary to dry well below 16 per cent water in order to grind the material without continually clogging the grinder and screens. The water content can then be raised to the proper point by spraying, using a special type of atomizer which prevents the formation of any but the very finest droplets.

MODIFICATIONS TO SECURE GREATER HARDNESS

It is possible that the soda lime above described may not be sufficiently hard for certain special industrial purposes. The hardness can easily be increased, however, though only at the expense of absorptive efficiency, as previously pointed out. A wide variety of possible binding agents have been tried out, with the result that the addition of 1 or 2 per cent kieselguhr was found to give the greatest increase of hardness for a given decrease in absorptive efficiency. The binding action is probably due to the formation of sodium silicate during drying, but when a similar increase in hardness was obtained by adding sodium silicate direct, or by adding a brand of lime containing reactive silica, the decrease in absorptive efficiency was much greater—apparently due to clogging the pores of the granules, which in the case of kieselguhr is largely offset by the increased porosity which it gives.



Incomplete results indicate that if 2 per cent kieselguhr is used the optimum alkali content is about 3 instead of 5 per cent.



VAPOR PRESSURE *vs.* WATER CONTENT

In order to work out the best drying conditions for the soda lime, and also to determine what water content would be produced by exposure to air of any definite humidity, it seemed desirable to determine the vapor pressure-water content curve of the soda lime for different temperatures. This work was done by Prof. G. P. Baxter and his associates at Harvard University, with the results shown in Plate VII. While the *absolute* vapor pressure changes quite rapidly with temperature, the *relative* vapor pressure (per cent of that of pure water at the same temperature) increases but very slowly.

It will be noted that although the army soda lime contains only 1 per cent alkali, it holds its water more tenaciously than the 4 per cent alkali industrial soda lime. This is undoubtedly due to the presence of the sodium permanganate and kieselguhr in the former. The army soda lime composition was carefully controlled so as to maintain its optimum water content (11 to 12 per cent) under the average prevailing humidity in France (70 per cent). It would appear from this that the 4 per cent alkali industrial soda lime is not sufficiently hygroscopic to maintain its optimum water content under ordinary weather conditions in this country, but a few tests on the 5 per cent alkali material recommended herein indicate that it approximates the army curve very closely.

COMPARISON WITH ORDINARY COMMERCIAL MATERIALS

In view of the great advantage of low alkali contents from practically every standpoint, it is surprising to find that of the five principal (if not the only) brands of soda lime on the market up to June 1918, four had an alkali content in the neighborhood of 40 per cent, and the other contained about 20 per cent. All appeared to be made by essentially the old type fusion process previously mentioned. These commercial brands were carefully tested on all the standard gases, together with samples from large-scale batches of soda lime made at the Gas Defense chemical plant in accordance with the three formulas described in this article. The results are summarized in Table 2, the commercial samples being designated A, B, C, D, and E. All were screened to the same mesh before testing.

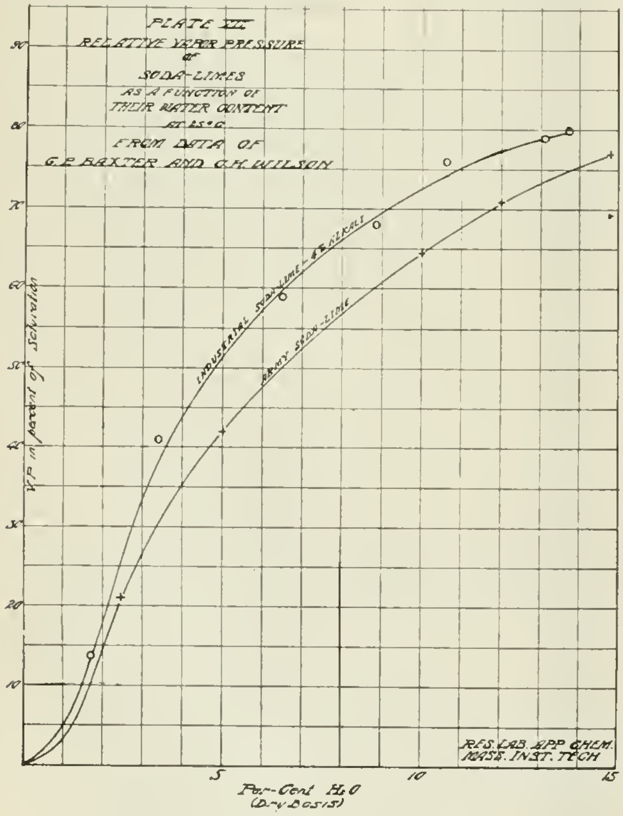
TABLE 2—COMPARISON OF COMMERCIAL SODA LIME WITH ARMY AND INDUSTRIAL SODA LIMES

Conditions of Tests (except CO_2—see Plate III)

Mesh of Soda Lime	8–14
Depth of Absorbent Layer	10 Cm.
Rate of Flow per Sq Cm. per Min.	500 Cc.
Relative Humidity of Air	50%
Temperature	20° C.
Concentration of Gas	See Table

SAMPLE	H_2O Per cent	NaOH Dry Basis Per cent	—Minutes to 99% Efficiency— 1% $COCl_2$	0.1% CCl_3-COOCl	0.1% CNCl	1% SO_2	0.1% Cl_2	2% CO_2	To 50% Efficiency Grams CO_2 per Grams Soda Lime
A	14.8	41.5	15	98	5	19	41	17	0.029
B	1.2	21.0	4	24	0	15	14	14	0.024
C	14.4	43.4	17	86	8	23	44	34	0.063
D	2.1	40.8	6	35	0	13	18	12	0.020
E	11.7	39.9	13	70	5	20	35	26	0.041
Army S. L.	11.5	1.0	25	130	3	24	30	15	0.033
Industrial S. L.	12.0	5.0	36	230	30	65	62	70	0.240
CO_2 S. L.	17.6	4.0	26	165	20	52	43	110	0.320

These results show very clearly the great inferiority of the high alkali materials as compared with those containing only 4 or 5 per cent NaOH. Even the very hard, low-alkali army soda lime is better against most gases than the commercial brands. The industrial soda lime shows its greatest degree of superiority against weakly acid gases, such as CO_2, and against high concentrations, where great activity is the prime requisite. The high-alkali soda limes show up relatively most favorably against chlorine, as would be expected, though even here the low-alkali product is fully 50 per cent better. In the case of CO_2, the CO_2 soda lime is four times as good as the best commercial product which was specifically recommended for that purpose.



The quantitative results against gases are, however, by no means the most favorable basis of comparison for the low-alkali soda limes. A canister filled with 8 to 14 mesh high-alkali (41 per cent) soda lime was found to deliquesce and clog so badly during one-half hour's service on a moist day that it was impossible to continue to breathe through it. A strong solution of caustic soda is produced almost as soon as the absorbent comes into contact with moist air, and this attacks the cotton pads, clogs the wire screens, runs out through the valve, and in general renders such materials hopeless for use in gas-mask canisters. If larger granules are used, as is customary for such materials, the clogging does not take place so rapidly, but the gas absorption is much less efficient.

RESULTS OF PRACTICAL TESTS

The CO_2 soda lime described above was designed primarily for the absorption of CO_2 on submarines, and gave excellent results in service during the latter part of the war; in fact, the much greater efficiency of the new material made possible submergence periods four times as long as had previously been possible.

Several canisters were made up for the absorption of CO_2 in self-contained oxygen breathing apparatus. Volume for volume the new material lasted 3.8 times as long as the best now in service, and had the further advantage of delivering a much cooler gas to the wearer—the high-alkali soda limes heating the air, due to the absorption of moisture. The only disadvantage was the high humidity of the effluent air, but it was found possible to reduce this without great loss in efficiency by using 7 per cent alkali and 14 per cent H_2O—a high water content not being necessary in this case, because of the high humidity of the air coming to the absorbent.

The material has been used with great success for CO_2 absorption in human calorimeters at the Rockefeller Institute, Cornell Medical School, and Johns Hopkins University. It was found that the resistance through the absorption box could be reduced 60 per cent, and replacements made much less frequently than with the previously used absorbents.

The Department of Agriculture and one of the Columbia University laboratories have used the CO_2 absorbent for CO_2 determinations in steel analyses and organic combustions with extremely satisfactory results. This laboratory is now undertaking a study of the most efficient composition for the somewhat special case of steel analyses.

The 5 per cent alkali gas absorbent, together with varying amounts of charcoal, has been filled into several hundred experimental canisters, tested against a variety of gases, and found to average fully twice as good an absorbent as the same sized canister filled with the standard army soda lime-charcoal mixture. Service tests of the canisters showed no serious tendency to produce fines or channel, even after very rough handling, provided they were properly filled and held in position by the customary springs.

CONCLUSION

In conclusion, it appears that the above-described soda limes are a great improvement, both in stability and efficiency, over any of the customary types. The best composition for a variety of different purposes has been carefully worked out, and found entirely satisfactory under actual service conditions. The single objection to the product is its complicated method of manufacture, which is admittedly much more difficult and expensive than the customary simple processes. It is nevertheless felt that the new product can be made more cheaply per unit absorption than any of the previous materials, and will find a wide use wherever a high degree of absorptive activity and capacity is desired.

ACKNOWLEDGMENTS

The writer desires to express his appreciation of the careful work of Lieut. W. B. Ross and his assistants at American University in carrying out most of the experiments on which this article is based; and also of Dr. C. P. McNeil and Lieut. E. P. Brown, who verified the majority of the conclusions by large-scale experimentation in the Gas Defense chemical plant at Astoria, L. I.

THE JELLY STRENGTH OF GELATINS AND GLUES

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Received July 1, 1920

For several uses of gelatins and glues the tensile strength of the jelly is regarded as the most important test.[1] This has been particularly the case in rating glues, but it is also of considerable importance for gelatins used in photography and in the paper industry. Analogously to the "wet strength" of papers, the jelly strength of a gelatin is obviously of primary importance for its use in photographic operations. This is perhaps even more the case on account of the increasing use of flexible film support in place of the rigid glass base.

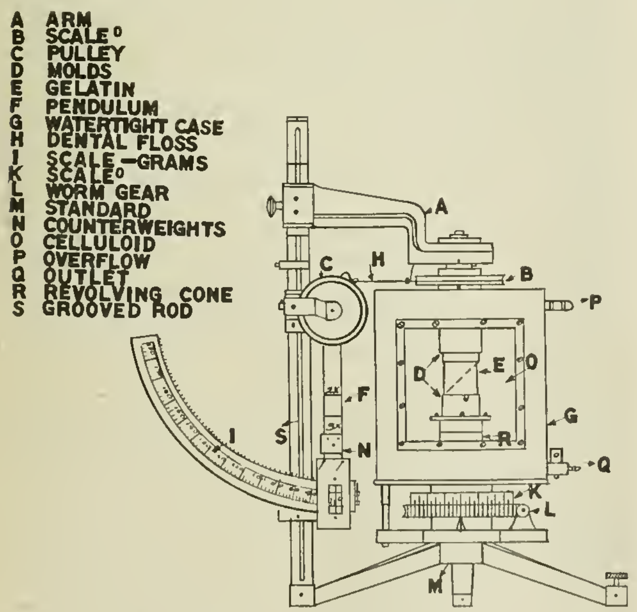

Fig. 1—Diagram of Jelly-Strength Testing Machine

The method originally recommended for practical commercial purposes was that of measuring, or rather comparing, the resistance of the jelly by means of the finger, grading the jellies by comparison with a set of arbitrary standards. Although no doubt satisfactory for many commercial purposes, the purely comparative and very subjective nature of the test obviously made it desirable to have a method giving values independent of comparison with an arbitrary standard, and objective in character.

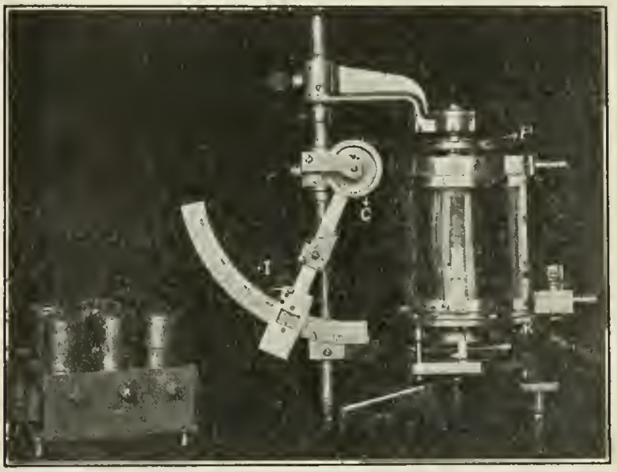

Fig. 2

To this end various methods[1] have been devised. Practically all consist of mechanical imitations of the "finger test," substituting some type of loaded plunger for the finger, and determining the load necessary to break through the jelly surface. As pointed out by Alexander,[2] all methods which depend upon the breaking or compression of a jelly in open glasses or molds are subject to errors due to the formation of a "skin," of greater or less thickness (depending upon humidity, temperature, etc.), and in some cases to errors from variations of diameter, giving a surface of uncertain area. To avoid these troubles, Alexander[3] has devised a tester operating on jelly blocks free from containing walls, and with the surface skin at the bottom.

A further defect in the methods referred to is that the stress applied affects both elasticity of bulk and elasticity of figure.

TENSILE STRENGTH UNDER TORSION

For more exact testing, and particularly for research on the properties of gelatin jellies, a jelly-strength testing machine operating by torsion has been devised by one of the writers (S. E. Sheppard). In seeking for correlation between viscosity coefficients and elasticity coefficients or moduli, it is desirable that the elastic values, *e. g.*, limit of elasticity and tensile strength, should be obtained for pure shear. This condition is secured by submitting cylinders of the material to be tested to torsional stress.[4]

The construction and mechanism of the instrument will be readily grasped from the diagram (Fig. 1), and the photograph (Fig. 2).

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[1] R. L. Fernbach, "Glues and Gelatins," D. Van Nostrand Co., New York, **1906**, p 45.

[1] See bibliography at end of paper. A detailed description of the methods is given in a forthcoming monograph on "gelatin" by one of the authors.

[2] "Proteins," in Allen's "Commercial Organic Analysis," 4th Edition, Vol. VIII, p 607 (Blakiston, Philadelphia, 1913).

[3] *J. Soc. Chem. Ind.*, **27** (1908), 459; also U. S. Patent 882,731

[4] See textbooks on Strength of Materials.

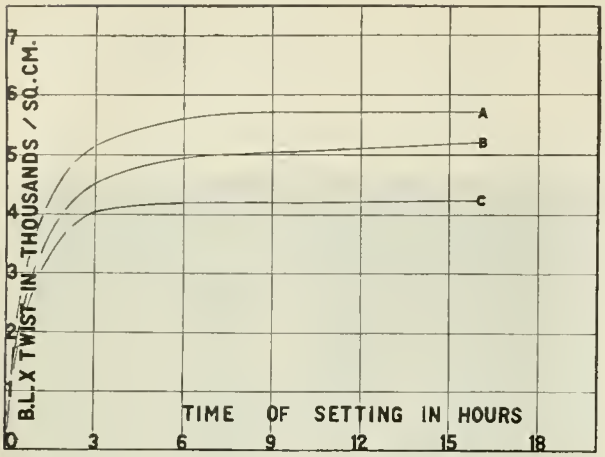

Fig. 3

GENERAL CONSTRUCTION AND OPERATION

The jelly is cast in a cylindrical mold having a split jacket removable after the test cylinder has been fixed in position in the instrument. In operation the jelly cylinder is twisted at a uniform rate by rotating the base at constant (angular) speed. This is effected by a worm drive, operated either by hand, or, where greater accuracy at low speeds is required, by a constant-speed electric motor. The circular base is graduated in degrees—Scale K—and the upper head of the "test cylinder" also carries a circular scale graduated in degrees—Scale B. One of the feet of the tripod base carries as a standard a steel rod grooved on opposite sides for its entire length. A short section at the top is free to rotate. This grooved standard carries an arm (Fig. 1) which is free to move up and down except as fixed by an adjustable setting collar, but which cannot rotate except when in position on the top section of the standard. This arm carries the upper "grip" for the jelly cylinders, which is rigidly connected with a pulley revolving freely on a ball race. The pulley (about 2.5 in. in diameter) carries Scale B. The grooves in the standard bring the pulley and the upper grip into perpendicular and centered alignment with the lower grip, the pulley wheel connecting, as shown, by a silk or fine chain cable with a lever, moving, as shown, along a calibrated scale, I. The lever or pendulum carries a set of pawls running lightly over the ratchet on the scale and keeping it from dropping back from any position to which it has been raised. The load of this counterpoise can be altered by placing jockey weights on the bob, so that multiplying factors of two and three times the scale readings are obtainable. The actual range with the first instrument constructed is from 10 to 550 g The "breaking load," W, is obtained from the limit position reached on the Scale I; the "twist" from the difference K′—B′ between the readings of the scales K and B at the moment of break.

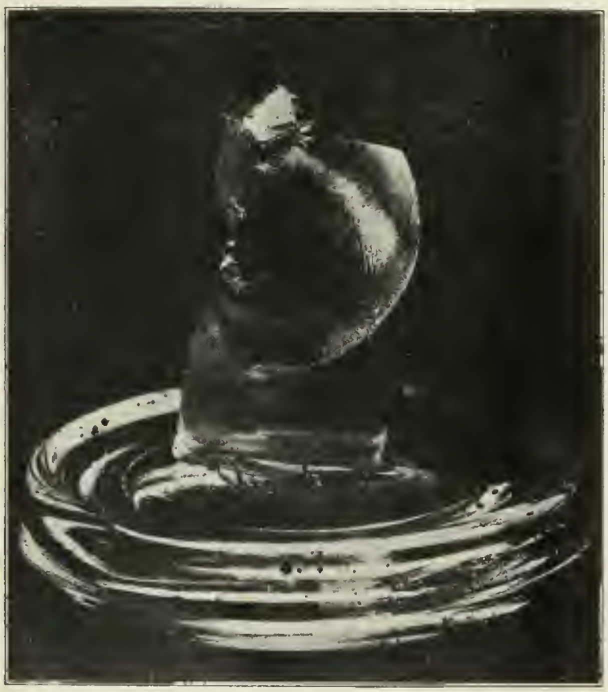

Fig. 4

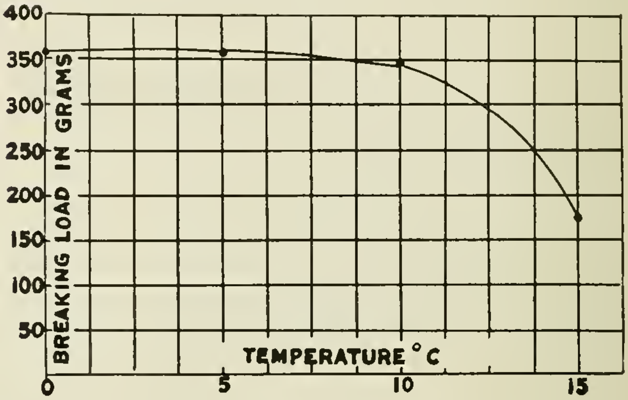

Fig 5

GRIPS AND MOLDS—It is desirable in any test of the strength of materials that the dimensions of the test piece be as definite as possible, and that the portions gripped do not affect the result. We find that this may be secured very simply with glue and gelatin[1] by filling the grips just flush with their ends with wood, the surface of which has small transverse grooves cut on it. The grooving not only increases the surface available for adhesion, but also facilitates molding free from air bubbles.

In filling the molds it is necessary to avoid formation of air bubbles, particularly at the interface of the wood and the jelly. After the side pieces are fitted on the bottom grip of the mold (Fig. 2) and this placed in the clamp shown in Fig. 2 (which insures a tight fit and no leakage), the gelatin solution, at about 40° C., is poured in until it just forms a meniscus at the top of the side plates. The upper grip is now carefully pushed across in the direction of the grooves, thus allowing air to be displaced. It is then pushed down into the mold, the excess gelatin solution and residual air being displaced through vent holes in the wooden core.

[1] For information on this subject the author has to thank Major Taylor, R. A. F., who has found in experiments with gelatin models of shafts that gripping by adhesion gives the least "end" error.

CHILLING THE TEST SPECIMENS—Experiments in chilling the test cylinders showed that after 3 hrs. at 0° C., little or no further increase in strength occurred (Fig. 3).

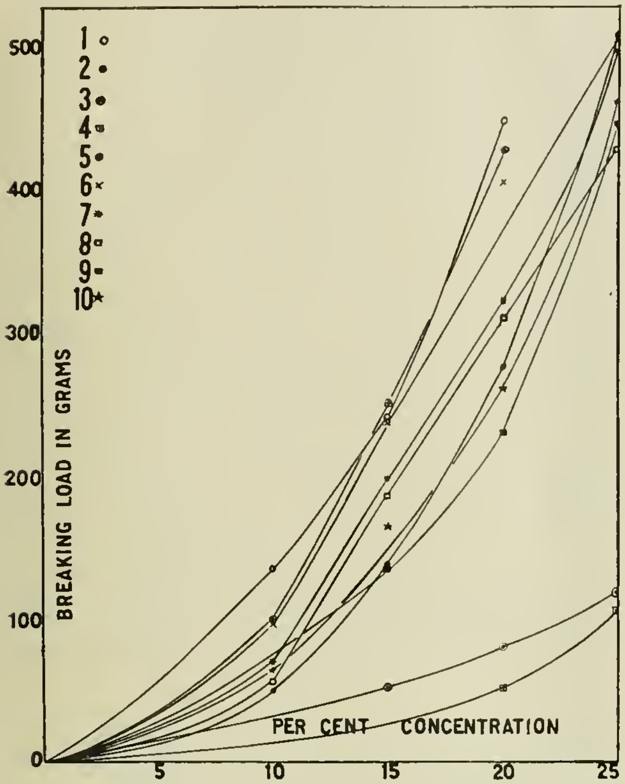

Fig. 6a—Comparative Jelly-Strength Tests

Samples 1, 2, 3, 4, 6, 7, 9 were American; 5, 8, 10, German gelatins

MAKING THE TEST—The entire mold is inserted in the lower clamp of the instrument, and the rotatable arm carrying the upper grip or clamp is swung around and fastened to the top of the mold by set screws. The Scales K, B, and I are all set at zero. The sides of the mold are then split off and the twisting started. This is stopped immediately on completion of a "break," and the angular difference K′—B′ read off, as also the breaking load on I. It is desirable to note also the character of the break. This should be a helical cleavage, of an angle of 45°, extending from the base to the upper end of the jelly column, with no sign of imperfect adhesion (Fig. 4).

Imperfect adhesion, which seldom occurs if proper precautions are taken, in filling and casting, should lead to rejection of the sample and repetition of the test. There are six molds in the set, but usually two or three check values are sufficient, allowing two or three different gelatins to be tested simultaneously. Apart from imperfect adhesion, however, a jelly may break off "short," corresponding to a low angle of twist and a brittle or crumbly structure.

EFFECT OF TEMPERATURE—Experiment showed that, after forming a jelly at 0° C. for 3 hrs., and then bringing it to a higher temperature and testing at that temperature, the "strength" did not alter materially till a temperature above 10° C. was reached. Above this point the jelly strength rapidly diminished (Fig. 5).

For experimental control of the temperature there is provided a water-tight jacket, revolving with the base and having transparent windows to facilitate observation, as shown in Fig. 2.

EFFECT OF CONCENTRATION—The relation of jelly strength to concentration is very important in making comparisons between different gelatins and glues. Although the jelly strength in any case increases more or less rapidly with the concentration, different gelatins differ considerably in this respect, as is shown in Fig. 6, where the curves of "breaking load" plotted against "concentration" frequently cut. Here concentration is based on air-dry gelatin. Consequently, according as comparisons were made below, at, or above the concentration where the curves cut, the one gelatin would be regarded as having lower, equal, or greater jelly strength than the other. For complete comparison it would be necessary to compare the areas enclosed by the breaking-load concentration curves from 0 to 100 per cent (based on dry gelatin). As this is not practicable, more or less arbitrary methods of comparison must be adopted. For some purposes we have taken the jelly-strength value of a photographic gelatin or paper gelatin as the slope $\Delta W/\Delta c$ between concentrations of 10 and 25 per cent (Fig. 7). As the actual expression for jelly strength instead of the breaking load, W, it appears better to use the value

$$S = \frac{\text{Breaking load} \times \text{per cent twist}}{\text{Cross-section area}},$$

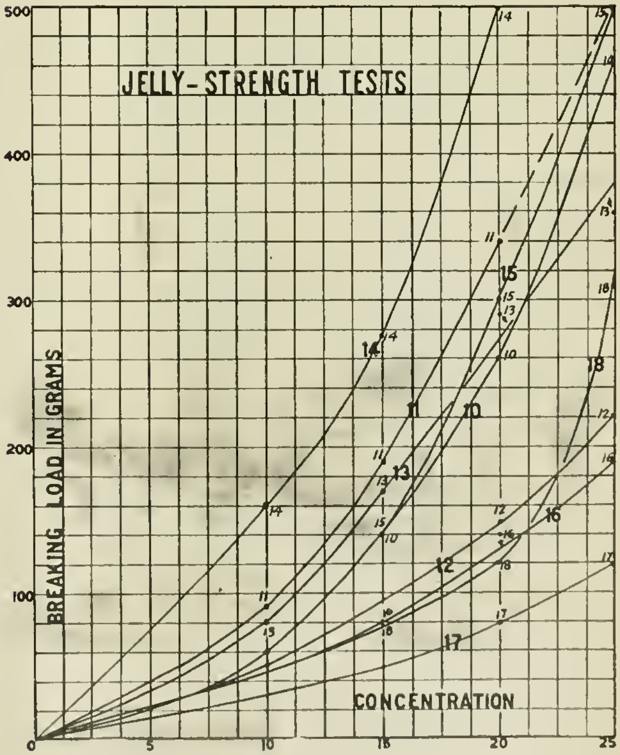

Fig. 6b—Jelly-Strength Tests

Sample 10, soft German; 11, hard German; 14, hard German (different brand); 15 English; 12, 13, American gelatins; 16, 17, 18, American glues and we have for the present taken this value as measuring the jelly strength in our investigations of the effect of heat treatment, electrolytes and non-electrolytes, etc., upon the properties of gelatin jellies.

RELATION OF JELLY STRENGTH TO TENSILE STRENGTH OF GLUE JOINTS

While our investigation was principally directed to the study of gelatins, it appeared of interest to ascertain whether correlation exists between the jelly strength of a gelatin or glue, and the tensile strength of the dry gelatin or glue, particularly as used in glued joints. It has already been stated by Gill[1] that the viscosity, the jelly strength by the plunger method of Lipowitz, and the tensile strength of glues stand in no definite relation to each other. As we were not able at this time to make direct test of the tensile strength of glued joints, according to methods devised by Gill and others, we have only connected up the "bursting strength" of absorbent papers soaked in the various glue solutions and dried.[2] Instead of a Mullen paper tester we have used a cylinder in which the air pressure is steadily increased until the bursting point is reached and noted on a pressure gage.

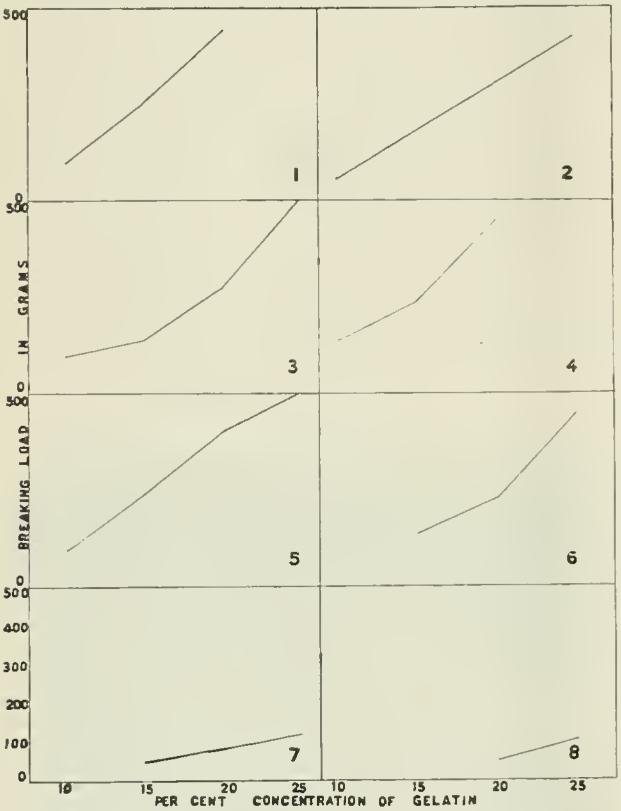

FIG 7—COMPARATIVE JELLY-STRENGTH TESTS
Samples 1, 2, 3, 4, 6 were American; 5, German; 7, 8, weak American gelatins

The general result of these tests is to confirm Gill's conclusion that jelly strength and "dry" tensile strength do not stand in a definite relation to each other. The fact that the jelly strength-concentration curves of different gelatins and glues often cut each other even below 25 per cent concentration is already sufficient to show that there can be no exact relation between the jelly strength at some one arbitrary concentration of air-dry gelatin, *e. g.*, 10 per cent, and the strength of the 100 per cent air-dry material. This is brought out in a generalized diagrammatic form in Fig. 8, which includes the case of a non-setting or "liquid" glue, having practically no jelly strength at any concentration below the air-dry state. If one and the same gelatin or glue be subjected to hydrolysis, reducing the jelly strength, the glue strength (as in-

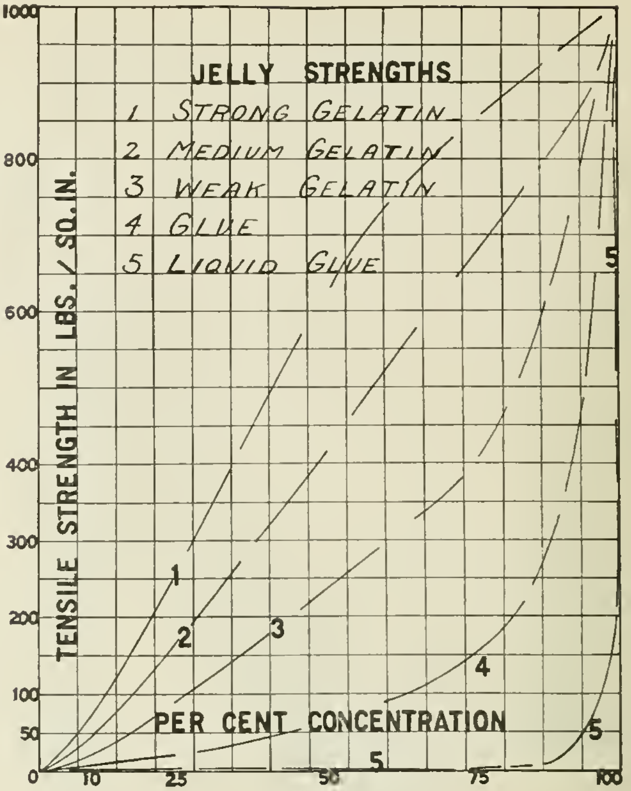

FIG. 8

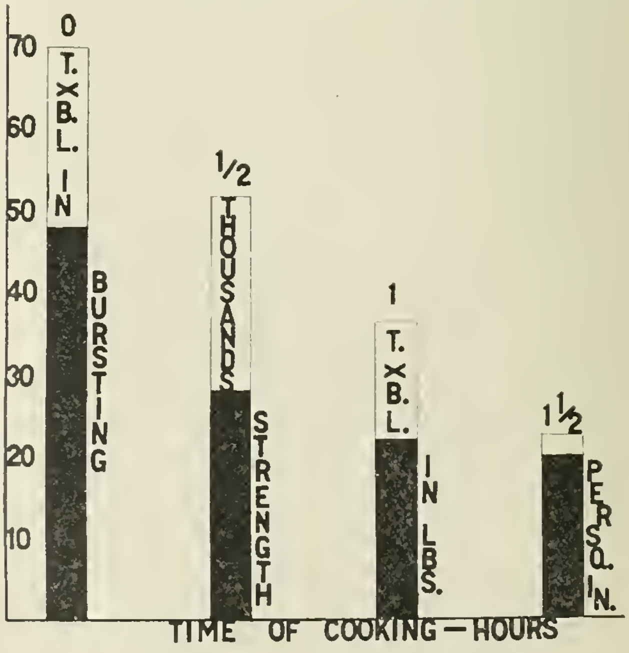

FIG. 9—COMPARISON OF JELLY AND BURSTING STRENGTHS

dicated by the bursting load) is also diminished, but not in simple proportion, as illustrated in Fig. 9.

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[1] THIS JOURNAL, **7** (1915), 102.

[2] Gill, *Loc. cit.*

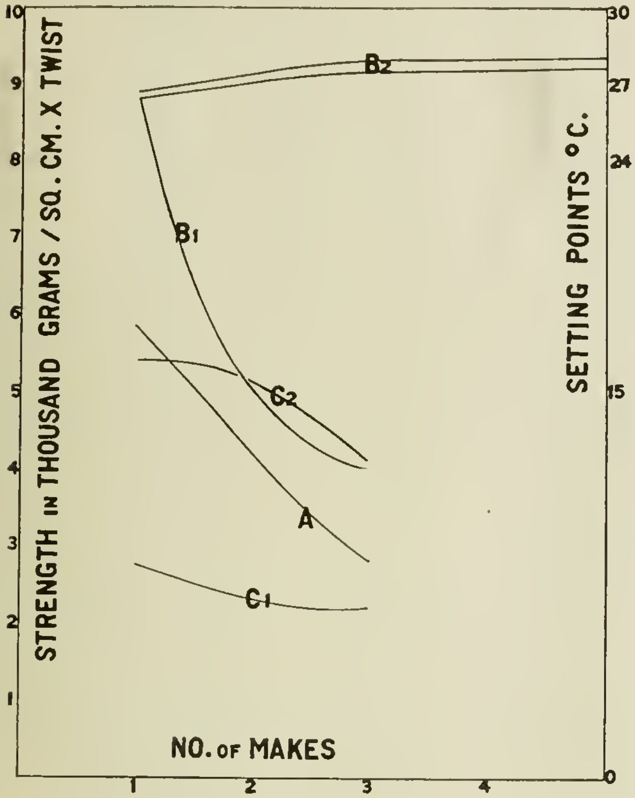

FIG. 10

Investigations on jelly strength are being continued with the object of obtaining satisfactory coefficients for testing of gelatins for photographic and other uses, and also of determining the influence of electrolytes, heat treatment, etc., on the jelly strength. It is known that the jellying powers of different gelatins are differently affected by remelting, and an example of this is given in Fig. 10. An automatic recording device is also in course of construction, so that determinations of the "elastic limit" and "proof resistance" may be measured from the *load twist* curves.

SUMMARY

1—A torsion dynamometer is described for determining the jelly strength of gelatin and glues under pure shear of molded cylindrical test pieces.

2—Both the "breaking load" and the percentage twist at break are determined; the product of breaking load × twist, divided by the cross section of the test piece, is taken as the jelly strength.

3—No simple relation holds between the concentration of gelatin and the jelly strength; furthermore, the curves relating these values for different commercial gelatins do not belong to a common family, and frequently cut each other. Hence, jelly-strength values determined for a single arbitrary concentration give a very arbitrary comparison of the jelly strengths.

4—There appears, consequently, to be no definite relation between the jelly strength, as a given concentration, and the glue-joint or tensile strength of a dry glue joint.

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GASOLINE FROM NATURAL GAS. IV—TEMPERATURE CORRECTION AND BLENDING CHARTS

By R. P. Anderson

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Received May 12, 1920

The topics discussed in the present article are:

(1) The correction of gasoline gravity and volume to a temperature base of 60° F.

(2) A chart for blending gasoline and naphtha.

COEFFICIENT OF EXPANSION OF GASOLINE

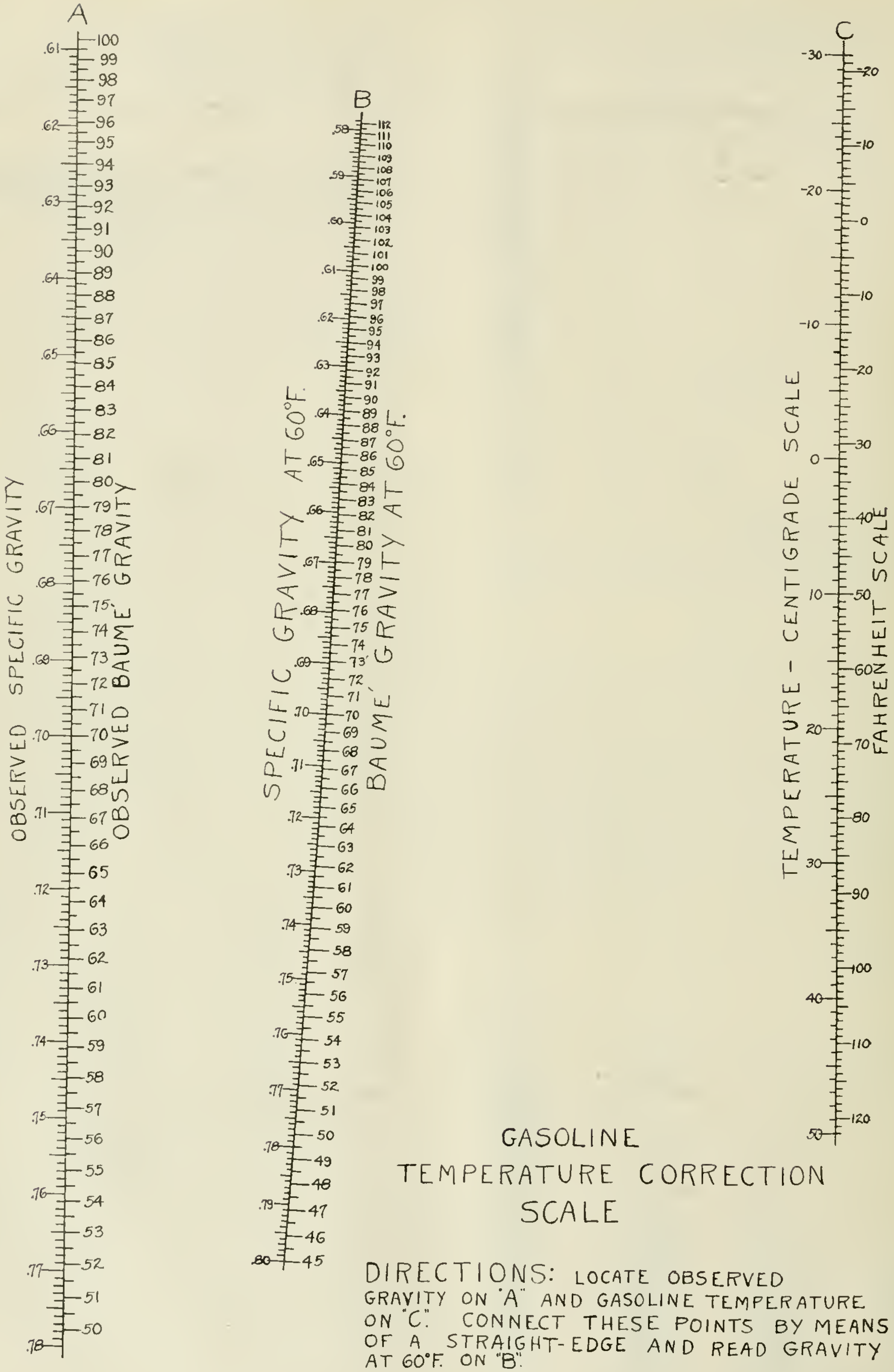
It is well known that the coefficient of expansion of petroleum oils increases as the specific gravity decreases. According to information contained in Table I of the Bureau of Standards *Circular* 57, the rate of this increase is not uniform. This is shown by the data contained in Table I of this article, where the change in specific gravity resulting from a change in temperature of 1° F. is given for specific gravities from 0.62 to 0.93. This information was obtained from *Circular* 57, by dividing the difference between the specific gravity at 120° F. and that at 30° F. by 90, the degrees difference in temperature. It will be noted that the rate of change in specific gravity for a change in temperature of 1° F. amounts to 0.23×10^{-5} for each 0.01 variation in specific gravity between 0.03 and 0.80, to 1×10^{-5} between 0.80 and 0.70, and to 0.57×10^{-5} between 0.70 and 0.63.

TABLE I

Specific Gravity at 60° F.	Change in Specific Gravity for 1° F.	Specific Gravity at 60° F.	Change in Specific Gravity for 1° F.
0.63	0.00053	0.79	0.00040
0.64	0.00052	0.80	0.00039
0.65	0.00052	0.81	0.00039
0.66	0.00051	0.82	0.00039
0.67	0.00050	0.83	0.00038
0.68	0.00050	0.84	0.00037
0.69	0.00049	0.85	0.00037
0.70	0.00049	0.86	0.00037
0.71	0.00048	0.87	0.00037
0.72	0.00047	0.88	0.00036
0.73	0.00046	0.89	0.00036
0.74	0.00045	0.90	0.00036
0.75	0.00044	0.91	0.00036
0.76	0.00043	0.92	0.00036
0.77	0.00042	0.93	0.00036
0.78	0.00041		

TEMPERATURE CORRECTION CHART

The nomographic chart shown in Fig. 1 was developed from the data in Table I for specific gravities below 0.80. Such a chart gives the user all of the necessary information for correcting the specific or Baumé gravity of gasoline to a temperature base of 60° F. on a single page of his notebook, a feature that is of importance when such information must be kept at hand; it makes it possible to correct degrees Baumé to specific gravity at 60° F., or *vice versa;* it permits the use of either Fahrenheit or Centigrade degrees without inconvenience, and it extends the lower temperature limit from 30° F. to −20° F.



GASOLINE
TEMPERATURE CORRECTION
SCALE

DIRECTIONS: LOCATE OBSERVED GRAVITY ON "A" AND GASOLINE TEMPERATURE ON "C". CONNECT THESE POINTS BY MEANS OF A STRAIGHT-EDGE AND READ GRAVITY AT 60°F. ON "B".

Fig. 1

Table II—Gravity Corrections at Low Temperatures

Observed Gravity Degrees Baumé

Degrees Baumé at 60° F.

° F.	67.0	68.0	69.0	70.0	71.0	72.0	73.0	74.0	75.0	76.0	77.0	78.0	79.0	80.0	81.0	82.0	83.0	84.0
—20	78.8	80.0	81.2	82.4	83.6	84.8	86.0	87.2	88.4	89.6	90.8	92.0	93.2	94.4	95.6	96.8	98.0	99.3
—18	78.5	79.7	80.9	82.1	83.3	84.5	85.7	86.9	88.0	89.2	90.4	91.6	92.8	94.0	95.2	96.4	97.6	98.8
—16	78.1	79.3	80.5	81.7	82.9	84.1	85.3	86.5	87.6	88.8	90.0	91.2	92.4	93.6	94.8	96.0	97.2	98.4
—14	77.8	79.0	80.2	81.4	82.6	83.8	85.0	86.1	87.2	88.4	89.6	90.8	92.0	93.2	94.4	95.6	96.8	98.0
—12	77.5	78.7	79.9	81.1	82.2	83.4	84.6	85.7	86.9	88.0	89.2	90.4	91.6	92.8	94.0	95.2	96.4	97.6
—10	77.2	78.4	79.6	80.8	81.9	83.1	84.3	85.4	86.6	87.7	88.9	90.1	91.2	92.4	93.6	94.8	96.0	97.2
— 8	76.8	78.0	79.2	80.4	81.5	82.7	83.9	85.0	86.2	87.3	88.5	89.7	89.8	92.0	93.2	94.4	95.6	96.7
— 6	76.5	77.7	78.9	80.1	81.2	82.4	83.6	84.7	85.9	87.0	88.1	89.3	89.4	91.6	92.8	94.0	95.2	96.3
— 4	76.2	77.4	78.6	79.8	80.9	82.1	83.2	84.4	85.5	86.6	87.7	88.9	89.0	91.2	92.4	93.6	94.8	95.9
— 2	75.9	77.1	78.3	79.5	80.6	81.8	82.9	84.1	85.2	86.3	87.4	88.6	89.7	90.9	92.0	93.2	94.4	95.5
0	75.6	76.7	77.9	79.1	80.2	81.4	82.5	83.7	84.8	85.9	87.0	88.2	89.3	90.5	91.6	92.8	94.0	95.1
2	75.3	76.4	77.6	78.8	79.9	81.1	82.2	83.3	84.4	85.6	86.7	87.8	88.9	90.1	91.2	92.4	93.6	94.7
4	75.0	76.1	77.3	78.5	79.6	80.8	81.9	83.0	84.1	85.3	86.4	87.5	88.6	89.7	90.8	92.0	93.2	94.3
6	74.7	75.8	77.0	78.2	79.3	80.4	81.5	82.6	83.7	84.9	86.0	87.1	88.2	89.3	90.4	91.6	92.8	93.9
8	74.4	75.5	75.7	77.9	79.0	80.1	81.2	82.3	83.4	84.6	85.7	86.8	87.9	89.0	90.1	91.3	92.4	93.5
10	74.1	75.2	76.3	77.5	78.6	79.7	80.8	81.9	83.0	84.2	85.3	86.4	87.5	88.6	89.7	90.9	92.0	93.1
12	73.8	74.9	76.0	77.2	78.3	79.4	80.5	81.6	82.7	83.8	84.9	86.0	87.1	88.2	89.3	90.5	91.6	92.7
14	73.5	74.6	75.7	76.9	78.0	79.1	80.2	81.3	82.4	83.5	84.6	85.7	86.8	87.9	89.0	90.1	91.2	92.3
16	73.2	74.3	75.4	76.5	77.6	78.7	79.8	80.9	82.0	83.1	84.2	85.3	86.4	87.5	88.6	89.7	90.8	91.9
18	72.9	74.0	75.1	76.2	77.3	78.4	79.5	80.6	81.7	82.8	83.9	85.0	86.1	87.2	88.3	89.4	90.5	91.6
20	72.6	73.7	74.8	75.9	76.9	78.0	79.1	80.2	81.3	82.4	83.5	84.6	85.7	86.8	87.9	89.0	90.1	91.2
22	72.3	73.4	74.5	75.6	76.6	77.7	78.8	79.8	80.9	82.0	83.1	84.2	85.3	86.4	87.5	88.6	89.7	90.8
24	72.0	73.1	74.2	75.3	76.3	77.4	78.5	79.5	80.6	81.7	82.8	83.9	84.9	86.0	87.1	88.2	89.3	90.4
26	71.7	72.8	73.9	75.0	76.0	77.1	78.2	79.2	80.3	81.4	82.4	83.5	84.5	85.6	86.7	87.8	88.9	90.0
28	71.4	72.5	73.6	74.7	75.7	76.8	77.9	78.9	80.0	81.1	82.1	83.2	84.2	85.3	86.3	87.4	88.5	89.6
30	71.1	72.2	73.3	74.4	75.4	76.5	77.6	78.6	79.7	80.8	81.8	82.9	83.9	85.0	86.0	87.1	88.2	89.3

Table II—Gravity Corrections at Low Temperatures (*Continued*)

Observed Gravity Degrees Baumé

Degrees Baumé at 60° F.

° F	85.0	86.0	87.0	88.0	89.0	90.0	91.0	92.0	93.0	94.0	95.0	96.0
—20	100.5	101.7	102.9	104.1	105.3	106.5	107.7	108.9	110.1	111.4	112.7	114.0
—18	100.0	101.2	103.4	103.6	104.8	106.0	107.2	108.4	109.6	110.9	112.2	113.4
—16	99.6	100.8	102.0	103.2	104.3	105.5	106.7	107.9	109.1	110.4	111.6	112.9
—14	99.1	100.3	101.5	102.7	103.8	105.0	106.2	107.4	108.6	109.9	111.1	112.3
—12	98.7	99.9	101.1	102.3	103.4	104.6	105.7	106.9	108.1	109.4	110.6	111.8
—10	98.3	99.5	100.7	101.9	103.0	104.2	105.3	106.5	107.7	108.9	110.1	111.3
— 8	97.9	99.0	100.2	101.4	102.5	103.7	104.8	106.0	107.2	108.4	109.6	110.8
— 6	97.5	98.6	99.8	101.0	102.1	103.3	104.4	105.6	106.7	107.9	109.1	110.3
— 4	97.1	98.2	99.3	100.5	101.6	102.8	103.9	105.1	106.2	107.4	108.6	109.8
— 2	96.7	97.8	98.9	100.1	101.2	102.4	103.5	104.7	105.8	106.9	108.1	109.3
0	96.3	97.4	98.5	99.7	100.8	102.0	103.1	104.3	105.4	106.5	107.7	108.8
2	95.8	97.0	98.1	99.2	100.3	101.5	102.6	103.8	104.9	106.0	107.2	108.3
4	95.4	96.6	97.7	98.8	99.9	101.1	102.2	103.4	104.5	105.6	106.8	107.9
6	95.0	96.2	97.3	98.4	99.5	100.7	101.8	102.9	104.0	105.1	106.3	107.4
8	94.6	95.8	96.9	98.0	99.1	100.3	101.4	102.5	103.6	104.7	105.9	107.0
10	94.2	95.4	96.5	97.6	98.7	99.9	101.0	102.1	103.2	104.3	105.4	106.5
12	93.8	95.0	96.1	97.2	98.3	99.4	100.5	101.6	102.7	103.8	104.9	106.0
14	93.4	94.6	95.7	96.8	97.9	99.0	100.1	101.2	102.3	103.4	104.5	105.6
16	93.0	94.2	95.3	96.4	97.5	98.6	99.7	100.8	101.9	102.9	104.0	105.1
18	92.7	93.8	94.9	96.0	97.1	98.2	99.3	100.4	101.5	102.5	103.6	104.7
20	92.3	93.4	94.5	95.6	96.7	97.8	98.9	100.0	101.1	102.1	103.2	104.3
22	91.9	93.0	94.1	95.2	96.3	97.4	98.5	99.5	100.6	101.7	102.8	103.9
24	91.5	92.6	93.7	94.8	95.9	97.0	98.1	99.1	100.2	101.3	102.3	103.4
26	91.1	92.2	93.3	94.4	95.5	96.6	97.7	98.7	99.8	100.9	101.9	103.0
28	90.7	91.8	92.9	94.0	95.1	96.2	97.3	98.3	99.4	100.5	101.5	102.6
30	90.4	91.5	92.5	93.6	94.7	95.8	96.9	97.9	99.0	100.1	101.1	102.2
32	....	....	....	....	....	....	96.5	97.5	98.6	99.6	100.6	101.7
34	....	....	....	....	....	....	96.0	97.1	98.1	99.2	100.2	101.3
36	....	....	....	....	....	....	....	96.7	97.7	98.8	99.8	100.9
38	....	....	....	....	....	....	....	96.3	97.3	98.4	99.4	100.5
40	....	....	....	....	....	....	....	95.9	96.9	98.0	99.0	100.1
42	....	....	....	....	....	....	....	....	96.5	97.6	98.6	99.6
44	....	....	....	....	....	....	....	....	96.1	97.2	98.2	99.2
46	....	....	....	....	....	....	....	....	....	96.8	97.8	98.8
48	....	....	....	....	....	....	....	....	....	96.4	97.4	98.4
50	....	....	....	....	....	....	....	....	....	96.0	97.0	98.0
52	....	....	....	....	....	....	....	....	....	....	96.6	97.6
54	....	....	....	....	....	....	....	....	....	....	96.2	97.2
56	....	....	....	....	....	....	....	....	....	....	95.8	96.8
58	....	....	....	....	....	....	....	....	....	....	....	96.4
60	....	....	....	....	....	....	....	....	....	....	....	96.0

It is somewhat inconvenient to employ, since a straight edge must be set on two points to enable the gravity at 60° F. to be read.[1]

The bend in the middle line of the nomograph at sp. gr. 0.70 is, of course, the result of the change in the rate of increase of the coefficient of expansion. Had the nomograph been constructed to include the higher specific gravities, there would also be a bend at sp. gr. 0.80. There may be some connection between this latter bend and the fact that specific gravities of paraffin hydrocarbons higher than 0.78 are due to the solution of solid hydrocarbons in liquids of lower specific gravity. It seems difficult, however, to offer any explanation for the bend at sp. gr. 0.70. In fact, that irregularity appears anomalous as a characteristic of the mixture of paraffin hydrocarbons constituting gasoline. It is possible that, if the experimental work could be performed with a sufficient degree of accuracy, a gradual increase in the rate of change of the coefficient of expansion would be obtained, instead of the sudden variation at sp. gr. 0.70 portrayed by the nomograph.

TEMPERATURE CORRECTION TABLE FOR LOW TEMPERATURES

By the use of the nomographic chart, the Bureau of Standards tables for correcting gasoline gravity for temperature have been extended from 30° F. to —20° F. for gravities that are ordinarily met with in

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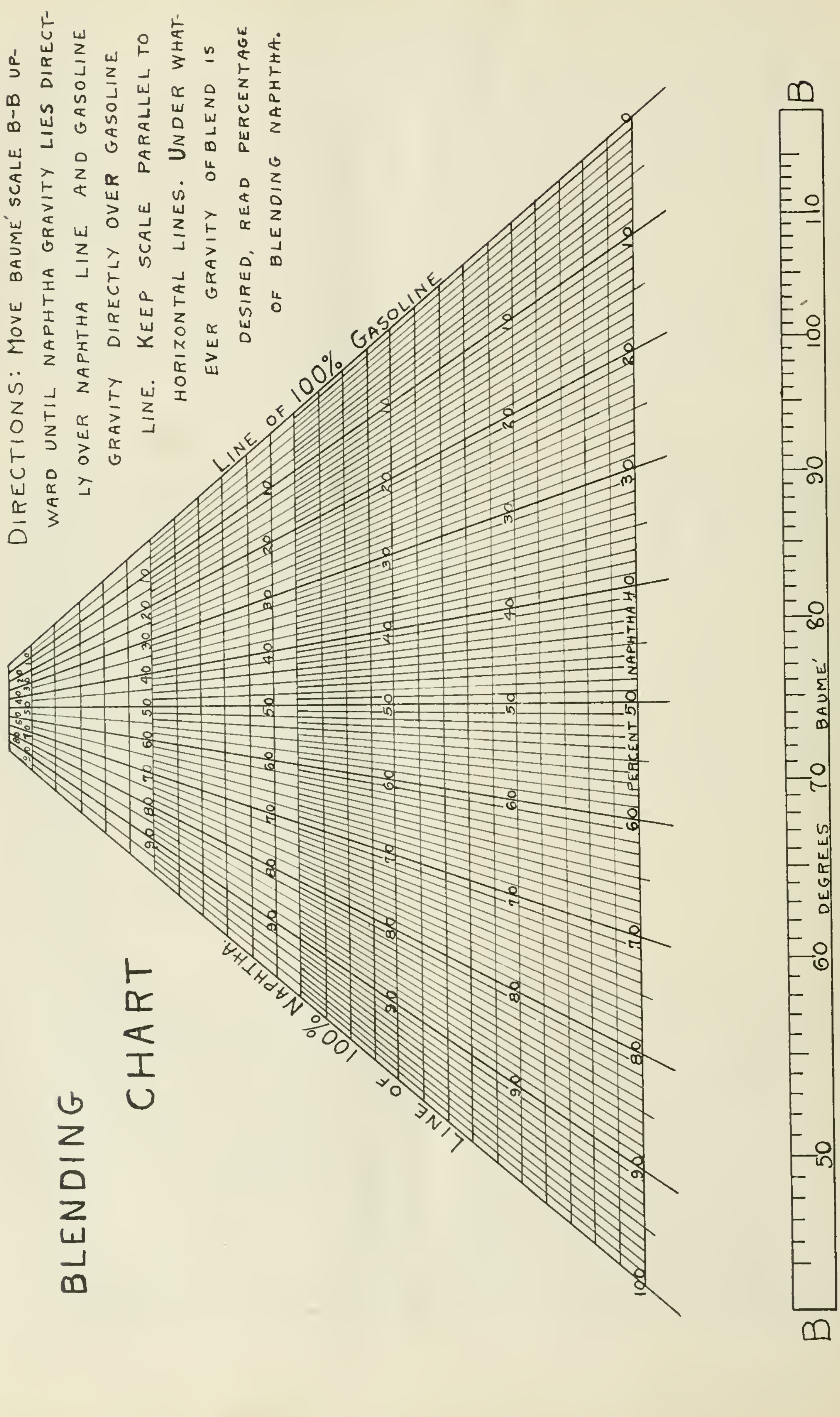
[1] Those who prfeer graphical methods to the use of tables will find that a series of lines prepared by plotting observed Baumé gravity against corrected Baumé gravity for every 5° or 10° between —20° F. and 120° F. gives an accurate and convenient method of correcting gravity for temperature in fairly small space.



BLENDING CHART

DIRECTIONS: MOVE BAUMÉ SCALE B-B UPWARD UNTIL NAPHTHA GRAVITY LIES DIRECTLY OVER NAPHTHA LINE AND GASOLINE GRAVITY DIRECTLY OVER GASOLINE LINE. KEEP SCALE PARALLEL TO HORIZONTAL LINES. UNDER WHATEVER GRAVITY OF BLEND IS DESIRED, READ PERCENTAGE OF BLENDING NAPHTHA.

Fig. 2

Table III—Gasoline Volume Factors (60° Basis)

Observed Temp. ° F.	Observed Gravity								
	50	55	60	65	70	75	80	85	90	95
	Factor to Correct Volume to 60° F.									
120	0.9705	0.9685	0.9665	0.9640	0.9620	0.9600	0.9580	0.9560	0.9540	0.9525
110	0.9750	0.9730	0.9715	0.9695	0.9675	0.9660	0.9645	0.9630	0.9630	0.9600
100	0.9795	0.9780	0.9765	0.9750	0.9735	0.9725	0.9710	0.9700	0.9605	0.9675
90	0.9845	0.9835	0.9820	0.9810	0.9800	0.9790	0.9780	0.9770	0.9760	0.9755
80	0.9895	0.9890	0.9880	0.9870	0.9865	0.9860	0.9850	0.9845	0.9840	0.9835
70	0.9945	0.9945	0.9940	0.9935	0.9930	0.9930	0.9925	0.9920	0.9920	0.9915
60	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
50	1.0055	1.0055	1.0060	1.0065	1.0070	1.0075	1.0075	1.0080	1.0085	1.0085
40	1.0110	1.0115	1.0125	1.0135	1.0140	1.0150	1.0155	1.0165	1.0170	1.0175
30	1.0165	1.0180	1.0190	1.0205	1.0215	1.0225	1.0235	1.0250	1.0260	1.0265
20	1.0225	1.0245	1.0260	1.0275	1.0290	1.0305	1.0320	1.0335	1.0350	1.0360
10	1.0290	1.0310	1.0330	1.0350	1.0370	1.0390	1.0405	1.0425	1.0445	1.0460
0	1.0355	1.0380	1.0405	1.0425	1.0450	1.0475	1.0495	1.0520	1.0540	1.0560
—10	1.0420	1.0450	1.0480	1.0505	1.0530	1.0560	1.0585	1.0615	1.0640	1.0665
—20	1.0485	1.0520	1.0555	1.0585	1.0615	1.0650	1.0680	1.0710	1.0740	1.0770

dealing with natural-gas gasoline. Table II contains this information, which may be considered an extension of the tables on pages 46, 47, and 48 of *Circular* 57. Such tables are valuable throughout the entire year in the manufacture of natural-gas gasoline, on account of the low temperatures that result from the release of pressure from condensates containing butane and propane.[1]

TEMPERATURE CORRECTION TABLE FOR VOLUME

Table III contains correction factors to be employed in correcting gasoline volumes to a temperature base of 60° F. It differs from Table III of *Circular* 57 in that Baumé degrees are employed instead of specific gravity, and the lower temperature limit is extended from 30° F. to —20° F.

BLENDING GASOLINE AND NAPHTHA

The widespread use of the Baumé scale in the gasoline industry complicates the problem of blending two grades of gasoline, or gasoline and naphtha, to produce a blend of a certain grade, as a result of the fact that the equivalent of 1° Bé. in terms of specific gravity is not constant throughout the Baumé scale. Different grades of gasoline blend without appreciable increase or decrease in volume, and consequently the composition of a blend of a given specific gravity can easily be computed, provided the specific gravities of the two constituents be known. If Baumé degrees are employed, they must be converted to specific gravity before such a computation can be made.

The necessity for such a computation can be obviated by the use of a suitable blending chart, such as the one designed by Netzen and printed by the United States Geological Survey, or such as the one shown in Fig. 2. The scale BB represents a specific gravity scale calibrated in degrees Baumé. If such a scale be superimposed on a scale of 100 equal parts, the number of equal parts lying between the Baumé gravity of the blend and the Baumé gravity of the high-gravity gasoline represents the percentage of the low-gravity gasoline, or blending agent. The system of converging lines provides a scale of 100 equal parts of variable length, thus providing a convenient means for determining the composition of blends of various gravities, with various gravities of the two constituents of the blends.

SUMMARY

1—The relationship between the coefficient of expansion of gasoline and its specific gravity, as exemplified by Table I, Bureau of Standards *Circular* 57, has been studied, and a nomographic chart based upon this relationship has been developed.

2—Temperature correction tables for Baumé gravity and volume have been extended from 30° F. to —20° F. to meet the needs of the natural-gas gasoline industry.

3—A blending chart for use in blending two grades of gasoline, or gasoline and naphtha, has been described.

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[1] To simplify the temperature correction for gravity, combination hydrometers have been employed in which the thermometers are calibrated to —20° F., instead of to 30° F., which is the case with the customary stock article. These special hydrometers were made by the Taylor Instrument Company. In the opinion of the writer, combined hydrometers intended for use in the natural-gas gasoline industry should have the lower limit of the thermometer extended to —20° F., and the approximate correction in degrees Baumé marked on the temperature scale should be abolished on account of the large error introduced by its use.

ADDRESSES AND CONTRIBUTED ARTICLES

BONE-BLACK AND DECOLORIZING CARBONS[1]

By W. D. Horne

National Sugar Refining Co. of New Jersey, Yonkers, N. Y.

Ever since Derosne introduced the use of bone-black in sugar refining in 1812, this agent has held a place of prime importance in the industry. The first cost of the material, which must be used in large quantity, the magnitude of the machinery necessary for handling it, and the complexity of the process have always been felt by those employing it, and have deterred from its use many who otherwise would be glad to avail themselves of this means of purifying and decolorizing juices, sirups, molasses, etc. Of late years the rapidly increasing price of bone-black, which has tripled in value, has further concentrated attention upon the need of rendering this material more efficient or of providing suitable substitutes. Many investigators have been active in making these attempts, in some cases without a sufficiently intimate acquaintance with the details of the requirements to enable them to work to the best advantage.

The object of the present paper is to direct attention to the desirable features of a decolorizing and purifying agent for use in sugar refineries and factories and to caution against undesirable properties.

BONE-BLACK AS A DECOLORIZER

The most desirable size of grain for bone-black in sugar refining is from about 16 to 30 mesh, and as it slowly wears down in use it is desirable not to allow more than 20 or 30 per cent of grains between 30 and 40 mesh to accumulate, or more than 5 per cent finer than 40 mesh. Artificial chars designed to be

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[1] Presented at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

used in column filtration should conform to these sizes. Hardness is also very important, to enable the grains to resist the abrasion of continued use. A satisfactory method of testing, described by the writer about 1891, consists of shaking 25 g. of the bone-black in a covered round tin can, 4 in. in diameter, with 6 marbles weighing 12.5 g. each. After 200 rapid swirling revolutions the bone-black is sifted through a screen having round holes one-sixtieth of an inch in diameter. The increase of dust as compared with that before the test indicates the dust formed by the attrition, and should not exceed about 2 per cent.

Bone-black improves with use for a few treatments, due to elimination of empyreumatic matter. It slowly deteriorates from choking of pores by carbon and mineral matter and by shrinkage from heating. It loses $CaCO_3$ and its power to reduce chance acidity of liquors. Attrition slowly wears it down so that it packs too closely for filtering viscous solutions at the usual density. This result is partly compensated for by sifting out the finer grains and dust, as well as by running liquors at reduced densities.

Carbon can be kept from choking the pores by regulated partial oxidation in revivifying, as in air-vented cooler pipes, or in the Weinrich decarbonizer. Mineral matter may be lessened by washing with dilute HCl, 1 to 2 per cent, but this action has only a temporary effect. Carbon can be built up by diminishing the washing prior to burning in the kilns of decarbonizers.

MECHANISM OF ABSORPTION WITH BONE-BLACK

The action of bone-black is partly chemical and partly physical. The calcium carbonate neutralizes acidity. Considerable heat is developed, as bone-black absorbs the coloring and other organic matter and the salts from a sugar solution. This is particularly strong in the first part of the filtration, endangering the sugar by caramelization and inversion, if filtration be too slow. The greater part of the color absorption appears to be mechanical, through the entanglement of the large molecules of the colloidal coloring matter in the fine cellular structure of the carbon. A filter no more than an eighth of an inch thick, properly prepared of fine fibrous material containing a mere central wash of bone-black carbon, will remove the color instantly from methylene blue, claret, or a raw sugar solution, which can be explained only on physical grounds. Mineral salts are absorbed through surface action largely, and Sir J. J. Thompson has attributed the activity of bone-black to this cause, modified by the internal and surface tensions of the solvents and the substances dissolved.

Patterson[1] has shown that the color absorption of bone-black is lodged in a certain dark brown humus-like substance, not pure carbon, which is soluble in concentrated sulfuric acid. Nitrogen plays a part in this color absorption. All bone-black contains some nitrogen, especially abundant in new char, which gives off great quantities of ammonia when being burned. This nitrogenous compound resists the heat of the kilns very persistently. The first liquors coming from the bone-black contain considerable ammonia, as evidenced by alkalinity to litmus, a yellow precipitate with Nessler's solution, and the development of an intense yellow color on the addition of traces of ferric chloride.

Bone-black does not decolorize cane juice satisfactorily, and at times it yields an inky or even a pinkish filtrate in refineries, owing, apparently, in both cases to the presence of polyphenolic compounds of iron.

There is thus an apparent partial failure on the part of bone-black to remove iron salts from solution. Indeed, what little iron a char may accumulate in filtering high-grade liquors will slowly be removed under the action of low-grade sugar solutions, as though the mineral salts in the latter exercised a specific iron removal. Since it is very desirable to have as little iron as possible in sugar solutions, this is a point for investigators to develop.

In washing the char after filtration, the absorbed impurities can be almost completely removed, but owing to the large amount of water required and the length of time necessary, the final removal is accomplished by means of burning. Washing with soda or other chemicals is not commonly used.

Lately, efforts have been made to activate old bone-black by subjecting it to the action of steam under high pressure, taking advantage of experience gained during the war in the preparation of gas-mask carbon. One of these treated bone-blacks gave interesting results that are typical of the influence of reaction. When used freshly it gave considerable color absorption from a dark sirup. After washing out the sugar solution and boiling up with 1.0 per cent hydrochloric acid and again washing, it showed no color absorption from a washed sugar liquor, but after boiling out with water containing 10 per cent of a saturated sodium hydroxide solution, and washing out, it showed a very decided power to absorb color from a washed sugar liquor.

Similarly, a carbon prepared by the concentration and roasting of an industrial waste solution, actually darkened a raw sugar solution, but after boiling this carbon with dilute hydrochloric acid and washing, it showed a marked color-absorbing power. This particular carbon, acid-treated, removed a slightly increasing percentage of color when fresh carbon was added to the filtrate from the first treatment. Boiling the used carbon in soda solution effected a further increase in the percentage of color absorption.

OTHER DECOLORIZING AGENTS

Stimulated by the desirability of a cheap and easily handled substitute for bone-black, inventors have prepared many compounds, generally carbonaceous, to take its place. Porous mineral matters such as kieselguhr, fuller's earth, brick granules, and so on, impregnated with molasses, gelatin or other carbonaceous, or carbonaceous and nitrogenous substances and burned in kilns, have been tried, with varying success. None of these has yet been entirely successful. They are either deficient in power to absorb impurities, or break down too easily under the wear and tear of use.

Another class of decolorizers has been developed by the action of heat and reagents on organized vegetable substances. Sawdust, impregnated with earthy and mineral bases and salts and intensely heated, generally in presence of steam, has produced, in the laboratory, some excellent decolorizers. Norit, Eponite, etc., prepared on commercial scales by secret processes, are apparently made from vegetable fibrous materials and are low in ash. Norit, the most widely known of these preparations, comes in a finely powdered condition and weighs but 16 or 17 lbs. per cu. ft. In use it is mixed with the sugar solution, heated, and filter-pressed directly, even in liquors of very heavy density. Thus the cumbersome filters of the bone-black system are replaced by filter presses, possessing the advantages of less size, weight, and cost. These carbons are generally ten to twenty times as efficient as equal weights of bone-black, suggesting that the 10 per cent or so of carbon in the latter is the only decolorizing substance present. This conclusion would be wrong, however, as bone-black that has been almost entirely decarbonized by burning still possesses considerable color absorbing power.

Here we have the suggestion that substances entirely different from carbon, but possessed of very fine cellular structure, are capable of development for this purpose.

The affinity of these decolorizers varies for different substances and the same impurity may be taken up in very different degrees by the various absorbents. Thus, one of the carbons was found to take up 90 per cent of the color from a dark solution prepared by heating invert sugar with lime, while it took up only 23 per cent of the color from a caramel solution prepared by heating sugar, and which, to the eye, exactly matched the lime-glucose solution. Some of the carbons, moreover, take up the dull grayish color from cane juice which bone-black fails to absorb, and their use is being urged for making refined sugar directly from cane juice.

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[1] *J. Soc. Chem. Ind.*, **22** (1903), 608.

SELECTIVE DECOLORIZING ACTION OF DIFFERENT AGENTS

Complete color removal is proportionally much more difficult than partial removal. For instance, a certain percentage of decolorizing carbon added to a raw sugar solution removed 50 per cent of the color, a similar percentage added to the filtrate removed only 25 per cent of original color, and a third treatment removed but 7 per cent. This suggests that in the complex of coloring substances present in a raw sugar there may be some which are more easily removed than others. Some further knowledge of this phase of the subject may be attainable through investigation of the effects of decolorizing agents on colors of different wave lengths. With this in view, a series of readings were made with the Hess-Ives tintometer on some specially prepared solutions, both before and after subjecting them to the absorbing action of two different decolorizing substances. The scale on the instrument was replaced by one devised by the writer to give a more exact index of the amount of light passing through the observed solutions. Having found that any particular amount of color solution gave a reading on the reversed scale of ten times the square root of the amount of color, the new scale was constructed with 1 coinciding with the original 10 (of the reversed scale) with 4 lying on 20, with 9 on 30, with 16 on 40, with 25 on 50, and so on, up to 100 on 100. Using this scale, the following results were obtained, expressed in terms of color transmitted, for 100 readings.

	100 Cc. Treated with					
MATERIAL	15 G. Bone-Black			0.5 G. Carbon		
Caramel	Red	Green	Blue	Red	Green	Blue
Original	97	78	25	97	78	25
Treated	99	95	80.5	96	88	62
Lime-Glucose						
Original	97	85	50	97	85	50
Treated	99.7	99.6	97.2	99.6	99.2	94

It is thus apparent that different colored substances require different decolorizing agents to yield the best results. It would seem, also, that successive treatments with different decolorizers might give greatly augmented decolorization, but thus far results have been disappointing. This field merits full investigation.

In refining, it is desirable to use about 100 lbs. of bone-black to 100 lbs. of raw sugar. This will remove about 25 to 35 per cent of the ash, about 35 to 45 per cent of the organic impurities, and about 75 per cent of the color. This involves several filtrations, and as the ash amounts to about 0.6 per cent of the raw sugar and the organic matter to about twice as much, while the weight of the coloring matter is but slight, the absolute amount of these substances taken up is always quite small. The decolorizing carbons in some cases succeed in removing as much color as 20 times their weight of bone-black will remove. The ash absorption is frequently not so good as in char work, slight as that is. Bone-black is used in filters 20 ft. deep, so that the liquor passing down comes successively into contact with numerous layers of fresh char, thus giving up all its color and producing for long periods a colorless filtrate, while a decolorizing carbon in powder added directly to colored liquor in a tank at once absorbs what color it can, and when this homogeneous mass is filter-pressed all the effluent is alike. For white sugar making, this is not so advantageous as the char method, and so we find a multiple decolorization and filtration coming into vogue.

Again, the wearing down of decolorizing carbon in use tends to give slow filtration, and, as it is not convenient to screen out the finer particles, a most ingenious contrivance has been developed by the General Norit Company to scrape off the accumulated deposit from the filter leaves continually, so that the filtration may continue in the most unobstructed manner.

Revivification can be carried on by chemical means in the case of carbons much more easily and safely than in the case of bone-black, and this field presents interesting undeveloped possibilities.

Decolorizing carbons of fine properties have been made from quite a number of waste materials and some very cheaply. The desideratum is one cheap enough to throw away after using once, and which will absorb ten to twenty times as much color as bone-black, and ash and organic impurities in proportion. This may not come, but the advance has been so rapid we may not unreasonably expect to see some approach to it in the not distant future.

RECENT WORK ON DECOLORIZING CARBONS

The subject of decolorizing carbons is a large field in itself, and although much very good work has been published on it of late it can only be touched upon here.

Chaney has shown[1] that all primary amorphous carbon consists essentially of a stabilized complex of hydrocarbons absorbed on a base of active carbon. These primary carbons as such do not possess a high specific absorptive power, the active carbon having been saturated by the hydrocarbon absorbed by it. The process of activation must, therefore, consist fundamentally in the separation and removal of the hydrocarbons from the active carbon. This active modification of carbon is formed whenever carbon is deposited at relatively low temperatures by chemical or thermal decomposition of carbon-bearing materials; in general, below 500° to 600° C.

Zerban has published in recent bulletins of the Louisiana Experiment Station most interesting results in regard to the preparation and properties of these carbons. Bradley[2] has recently published an excellent resumé of his results in the study of the properties of Norit. These and other pioneers have shown the way in beginning to develop this method of preparing and using decolorizing carbons. It remains for the subject to be followed up industriously to attain results that will amply repay all efforts in the investigations of these fascinating questions.

HISTORY OF THE PREPARATION AND PROPERTIES OF PURE PHTHALIC ANHYDRIDE

By H. D. Gibbs

E. I. du Pont de Nemours & Co., Wilmington, Delaware

Received July 1, 1920

A United States patent[3] recently granted, which claims *as an article of manufacture* "phthalic anhydride substantially chemically pure and having a melting point above 130° C., corrected" and "phthalic anhydride in the form of colorless, needle-like crystals substantially chemically pure and having a melting point above 130° C., corrected," raises the question of the history of the preparation and properties of pure phthalic anhydride, particularly of the melting point. As will be shown later in this article, phthalic anhydride of a degree of purity which undoubtedly exceeds that of the product described in this patent was prepared and described at least as early as 1902 by Van de Stadt,[4] and in 1919 (prior to the date of filing of the application for U. S. Patent 1,336,182) by Monroe.[1] A process of manufacture by air oxidation (using vanadium and molybdenum oxides as catalysts) which yields a product in the form of "long, colorless, glistening needles,"[2] substantially chemically pure and having a melting point above 130° C. (corrected), has been described and patented by the author and C. Conover.[3]

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[1] *Chem. News*, **119** (1919), 283.

[2] *J. Soc. Chem. Ind.*, **38** (1919), 396

[3] U. S. Patent 1,336,182, Phthalic Anhydride, issued April 6, 1920, to C. A. Andrews, assignor to the Selden Company of Pittsburgh, Pa (Application filed October 14, 1919.)

[4] "Bernsteinsaüre und Phthalsaure-anhydrid in ihrem Verhalten gegenüber Wasser," *Z. physik. Chem.*, **41** (1920), 353. Van de Stadt's excellent investigation carried out in Amsterdam in collaboration with Prof. Bakhuis Roozeboom has not received the attention which it deserves, since it has been overlooked by compilers of the standard organic treatises, such as Beilstein's "Organische Chemie," Richter's "Organic Chemistry," and Meyer and Jacobson's "Lehrbuch der Organischen Chemie," and also by the compilers of Landolt-Börnstein's "Physikalisch-Chemische Tabellen." It is, however, noted in a recent American treatise, Seidell's "Solubilities of Inorganic and Organic Compounds," 2nd Ed., D. Van Nostrand Co., New York, **1919**, p. 491.

It was early observed in the development of the air-oxidation process that the product melted above 130° C., and the author stated in an article published in THIS JOURNAL in 1919:[4] "It is interesting to note that phthalic anhydride produced by this process is of a remarkable degree of purity. Naturally, it is free from chlorine or sulfur compounds, common impurities in phthalic anhydride as formerly found on the market." Monroe's investigation was, indeed, carried out at my suggestion while we both were employed in the Color Laboratory of the Bureau of Chemistry, in view of the confusion which existed in the earlier literature and in the standard organic treatises in regard to the melting point of pure phthalic anhydride, and in the absence of knowledge concerning Van de Stadt's earlier investigation, to which Doctor Monroe has called my attention since the publication of his own article.

In view of these facts, the fallacy of the claims of Andrews to *pure phthalic anhydride as an article of manufacture* is very apparent. It is difficult to conceive the grounds upon which such a patent could have been granted. In order that the matter may be clarified, the following summary of chemical literature bearing on these topics is presented:

Phthalic anhydride was discovered at least as early as 1836 by Laurent,[5] who prepared the acid by oxidation of naphthalene with chromic acid, and obtained phthalic anhydride by sublimation of the acid. The melting point of the sublimed product recorded by this observer is 105°, concerning which Lossen[6] states:[7]

> 105° Réaumur corresponds to 131° Celsius (Centigrade). It appears, therefore, that Laurent carried out his observation with anhydride which contained some acid, and used a Réaumur thermometer....... I found the melting point of anhydride which was prepared by one sublimation of phthalic acid to be 131° C....... The large discrepancy between this and the value given by Laurent (105°) led me to repeat the determination. I used for these experiments phthalic acid prepared in various ways, which had been completely transferred into the anhydride by long-continued heating to the boiling point (of the anhydride) .... A large number of very careful determinations gave *consistently* 128° C. as the melting point.

Although conclusions of little value from the viewpoint of exact thermometry may be drawn, one may not altogether exclude the possibility that pure phthalic anhydride of substantially correct melting point (compare Van de Stadt and Monroe, *Loc. cit.*) was thus obtained even at this early date by its discoverer, and in one instance by Lossen.

Anschütz[8] prepared phthalic anhydride by the dehydration of phthalic acid with acetyl chloride, and found its melting point to be 127° C. No exact conclusions in regard to the melting point of pure anhydride may be drawn from this observation, however, since the crystals of anhydride were purified merely by pressing between filter paper after removal of acetyl chloride by absolute alcohol.

Lachowicz[1] prepared phthalic anhydride by warming phthalyl chloride with lead nitrate; the crude substance was purified by recrystallization from benzene. The melting point found (128° C.) agrees with the previous values of Lossen and Anschütz, although the method of purification is scarcely sufficient to eliminate all impurities.

Stohmann[2] prepared phthalic anhydride by distillation of commercial phthalic acid, and recrystallized the crude sublimate from benzene-ligroin mixture. The observed melting point (128° C.) is in agreement with that found by the previous investigators, but this work is open to the same criticism, the phthalic acid prepared by chromic or permanganic oxidation of naphthalene in sulfuric acid solution (with mercury sometimes present as a catalyst in large-scale operations) is well known frequently to contain sulfur and chlorine compounds[3] which are not readily removed by sublimation or recrystallization.

Indeed the first recorded investigation in which sufficient precautions were observed to insure a chemically pure anhydride, and in which the observations were recorded to have been taken, not in the capillary tube manner, but with thermometer immersed in the melt, is that of Van de Stadt,[4] who states:[5] "I determined the melting point (of phthalic anhydride purified by distillation) in a sealed tube with sealed-in thermometer, since the substance absorbs water readily, and in this manner obtained the value 131.2° C." Van de Stadt examined the melting points of various mixtures of anhydride and water, and also determined the eutectic temperature of phthalic anhydride and acid to be 129.6°. He describes the experimental procedure in some detail:

> A mixture of 95 molecular per cent anhydride and 5 molecular per cent water was heated in a small open tube and the point of a final solidification observed. In spite of constant stirring, a large portion of the mass remained liquid after copious crystallization had occurred until the temperature of 129.8° was reached, when a second crystallization occurred, during which the thermometer remained constant ± 8 minutes between 129.8° and 129.6°. Another mixture of 90 molecular per cent anhydride with 10 molecular per cent water also gave such a (eutectic) point at 129.7°, and the same phenomenon was observed very markedly with a mixture containing 70 and 30 molecular per cent.
>
> We see, therefore, that two distinctly different crystal forms appear (first acid and then anhydride). The first crystals may be agitated with the mother liquor without further crystallization occurring; they are, therefore, phthalic acid, which had been dissolved in the molten anhydride. Microscopic examination led to the same conclusion.

It is to be noted that the eutectic obtained by the very careful work of Monroe for the system phthalic anhydride–phthalic acid exactly checks the work of Van de Stadt, and the latter article was not discovered by Monroe until after the publication of his own work.

In view of the above statements of facts, it is evident that the purest phthalic anhydride is not a new product.

NEW FIELDS OF PHYTOCHEMICAL RESEARCH OPENED UP BY THE CULTIVATION OF MEDICINAL PLANTS ON AN ECONOMIC SCALE[6]

By Edward Kremers

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The milling of half an acre of belladonna plants or the distillation of an acre of peppermint, when carried out by an observing scientist, ought to be productive of results, new in more ways than one. To the scientist who has conducted his experiments on a relatively small laboratory scale, the problems which confront him in milling or distillation may result in solutions new to him although old to the technologist. The fact, however, that the technologist does not record his experiences for the benefit of the scientist may make the observations of value to others if recorded. It is not to fields, new in this sense, that the writer wishes to draw your attention. The cultivation of medicinal plants on a semi-economic scale and the working up of the harvest, whether fresh or cured, present to the observing scientist fields that are new in quite a different sense. To some of these, selected at random, and the lessons already learned from them, the writer desires to invite your attention.

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[1] THIS JOURNAL, **11** (1919), 1116. (Read before the Dye Section, 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 2 to 6, 1919.)

[2] Monroe, *Loc. cit.*

[3] U. S. Patent 1,284,888. Process for the Manufacture of Phthalic Anhydride, Phthalic Acid, Benzoic Acid and Naphthoquinones, issued Nov. 12, 1918, to H. D. Gibbs and C. Conover (application filed May 12 1917); U. S. Patent 1,285,117. Process for the Manufacture of Phthalic Anhydride, Phthalic Acid, Benzoic Acid and Naphthoquinones, issued November 19, 1918, to H. D. Gibbs and C. Conover (application filed February 17, 1917).

[4] "Phthalic Anhydride. I—Introduction," THIS JOURNAL, **11** (1919), 1034 (Received Aug. 19, 1919).

[5] *Rev. Scient.*, **14**, 560; *Compt. rend.*, **21**, 36; *Ann.*, **19** (1836), 38.

[6] *Ann.*, **144** (1867), 76.

[7] Translated from the original German.

[8] *Ber.* **10** (1877), 326.

[1] *Ber.*, **17** (1884) 1283.

[2] *J. prakt. Chem.*, **40** (1889), 139.

[3] Gibbs, *Loc cit.*

[4] *Loc. cit.*; see also an earlier investigation by this author, *Z. physik Chem.*, **31** (1899), 250; Bancroft, *J. Phys. Chem.*, **1899**, 93; Ramsay and Young, *Trans. Roy. Soc. London*, **117**, I 103.

[5] Translated from the original German.

[6] Presented at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 2 to 6, 1919.

DIGITALIS

At the meeting of the SOCIETY held at Urbana in April 1916, the writer presented to the Division of Pharmaceutical Chemistry specimens of digitalis that had been milled and sifted with a set of analytical sieves. Whereas the No. 20 powder prepared for an eastern hospital contained 10 per cent of ash, the No. 100 powder had an apparent content of nearly 80 per cent. The apparent ash content of the intermediate powders varied correspondingly according to the degree of fineness. This observation afforded a ready explanation of the greatly varying records of ash content of digitalis as found in literature.[1] Since that time a microscopical study of leaves with hairy surfaces and of the soil adhering to such leaves has been made by Tschirch.

The first lesson to be learned from this experience was a simple mechanical method of purifying digitalis and other leaves (hyoscyamus, sage, etc.). This method has already been adopted by others.

A second lesson is one for the analytical and government chemist. The Wisconsin Pharmaceutical Experiment Station certainly had no commercial motives when it gave some of its digitalis to eastern hospitals, yet, with all the care exercised in cultivation and curing, a so-called crude drug had been produced that yielded about 25 per cent of apparent ash. A high ash content—and ash standards have again come into greater prominence—does not necessarily indicate adulteration, not even carelessness. It may be largely a matter of the character of the soil on which the foxglove has been raised, or a question of rains, quite beyond the control of the grower.

A third lesson is revealed in the possibility of controlling the process of milling so as to yield the largest percentage of coarse powder, provided, naturally, that such is the object of the miller.

A fourth problem was suggested at the Urbana meeting by the late Mr. Wilbert, who pointed out that if the apparent ash consists largely of clay, the occluding effect of this admixture may be such as to interfere with the therapeutic effect of the active constituents. The solution of the problem will be a joint one for pharmacist and pharmacologist.

Still another problem is met in working up the by-products of the milling room for pharmaceutical preparations of desired strength or, better still, of definite chemical composition. These problems have been attacked and it is hoped may form the subjects for separate reports.

HYOSCYAMUS

When the milling experience worked out in connection with digitalis was applied to hyoscyamus by our pharmacognosist, Dr. W. O. Richtmann, and his assistant, Mr. F. Bacon, a striking observation was recorded. The ash determination happened to be made in the open laboratory rather than in the hood. In the assay of the fine powder there resulted a smoke which caused the occupants of the room to cough. No such result had occurred when the coarse powders had been incinerated. A microscopical examination of the fine powder revealed that it consisted not only of soil particles, but also of innumerable leaf hairs. Hence, aside from the lessons already learned from the milling experience with digitalis, we have several additional lessons to record.

The first of these is that in the milling of drugs we may have a very convenient means of separation of plant organs for special investigation, chemical or otherwise.

Second, Dr. Richtmann has been of the opinion, based on field observations, that the attraction of the plant for the potato beetle—this season all of the second year crop had to be harvested early in May because the potato beetle, finding no potato vines, threatened to devour every leaf—is due to a peculiar odor of the leaf. What more natural, therefore, than to infer that these leaf hairs are the reservoirs in which are stored the possible aldehydes, which on being heated in the crucible caused the irritation of the throat. Already a preliminary distillation with water vapor of the fine powder, rich in plant hairs, as well as soil particles, has been made. It is expected that after the 1919 crop has been milled a sufficient amount of this fine powder will have been separated to make possible a careful study of this problem.

Last and possibly not least, if the odoriferous substances of the hyoscyamus that attract the beetles can be identified, it may be possible to attract the beetles to traps containing these substances and to save the crop for further growth.

PEPPERMINT

The cultivation of an acre of peppermint during the season of 1917 enabled the Station to initiate a series of experiments[1] in distillation. Mr. Norbert Mueller, the government expert, distilled the fresh peppermint harvested late in the summer of that season and Professor E. R. Miller, at the time chemist of the Station, cohobated the aqueous distillate which had been saved for that purpose. Suffice it here to call attention to the following points:

First, the additional oil obtained by cohobation amounted to about 10 per cent of the oil obtained by the first separation. This oil differs materially, quantitatively if not qualitatively, from the regular crude, *i. e.*, non-rectified peppermint oil, and hence invites special study.

Second, for every liter of oil separated a liter of water-soluble constituents was obtained by repeated cohobation, or, to put it in other words: For a thousand-acre peppermint farm we have been throwing away from one to two thousand liters of organic chemicals.

Third, whether or not these observations prove of economic importance, their biochemical significance is in no way diminished.

Just as the commercial drug miller has kept his experiences largely to himself, so the distiller of peppermint and other aromatic herbs has not infrequently kept his observations to himself. For the most part he has not found the time in the rush of the season to interrupt his commercial production and to indulge in experiment. At times also he has not been in a position to interpret properly such observations as he has made.

The distillation of plants and parts of plants in the production of volatile oils has proven one of the most satisfactory methods of isolation in phytochemistry. Yet in comparatively few instances have the less striking water-soluble volatile constituents received any attention whatever.

The experiment with peppermint could not be repeated in 1918 because of the winter-killing of the mint. During the present season, however, the aqueous distillate is again being collected for cohobation. During the season of 1917 Professor Miller collected the aqueous products of a number of distillations, and his results are soon to be published as a Station circular[2]

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[1] A compilation of ash determinations of vegetable drugs has been prepared by several students, but the voluminous manuscript has not yet been edited for publication.

[1] Wisconsin Pharmaceutical Experiment Station, *Circular* **9**

[2] University of Wisconsin, *Bulletin* **1024**

During the present season Roland E. Kremers, who carried out a number of distillations for the Station, has collected and cohobated the aqueous distillates of wormwood, tansy, peppermint, and milfoil. The aqueous distillates of *Monarda punctata* and *M. fistulosa* will be collected by D. C. L. Sherk, who will also supplement Professor Miller's study of *M. fistulosa* by a parallel examination of *M. punctata*.

If it required years of study to isolate and identify the oily constituents of plants, it will, no doubt, require years and years to study their water-soluble volatile constituents. If for years the writer has desired to devote to these latter constituents such attention as they seem to merit, he has also wanted, for the same length of time, to study those products which escape from the condenser and are not collected either in the separated oil or in the aqueous cohobate. The study of these escaping vapors will require, as experience has already shown, specially constructed condensers and absorbers. Thus will be trebled in size, as it were, this one field of phytochemistry.

In bringing to your attention some of our milling and distillation problems, the writer has not attempted to solve any milling or distillation difficulties from a technological point of view, but has desired to point out how large technological operations and the biochemical study of plants should work hand in hand for the advancement of plant chemistry.

A COMPARISON OF ACCURACY IN ANALYSIS OF METALLURGICAL MATERIALS DURING THE PAST TWENTY-FIVE YEARS

By E. D. Campbell and George F. Smith

University of Michigan, Ann Arbor, Michigan

Received June 5, 1920

It has been only a little more than 50 years since steel manufacturers realized the necessity of chemical control of their finished product, and the consequent necessity of knowing the composition of the various materials entering into the process, and the changes taking place during the various steps between the raw materials and the finished steel. During the 70's and 80's, chemists of many metallurgical companies developed a practice of exchanging carefully prepared and analyzed samples of steel and ores, in order to compare the accuracy of the results obtained by different chemists working on the same sample.

In February 1889, the late John W. Langley, in an address before the Engineering Society of Western Pennsylvania, advocated the preparation of a set of steels which should be analyzed by a number of leading chemists in different countries and should then constitute international standard steels. This idea Langley developed in a second paper.[1] Committees on analysis were formed in England, Sweden, the United States, France, and Germany. Some preliminary bulletins were prepared during the next three years and the results of the analyses, representing the work of the committees from the first three countries named, were published in the *Chemical News* for September 29, 1893.

It was the intention of the American committee, when the results of the analyses had been collected, to have the principal part of the American portion of the five international standard steels kept in some suitable depository, so that small samples could be distributed to such chemists as might be entitled to them. The chemical laboratory of the University of Michigan was selected as a suitable depository and the five standard steels were deposited there in September 1893.

Very little of this material was ever called for, and recently a large bottle of each of the five original international standard steels was sent to the Bureau of Standards to be kept because of their historic interest.

Although analytical chemists continued to feel the need of some means of determining the accuracy of analytical methods, and the variations which might be expected between different chemists working on the same material, it was nearly ten years later that the Bureau of Standards at Washington instituted a system of preparing carefully analyzed samples, which would cover a wider field than that of steel alone.

In the summer of 1895 one of the authors gave a paper before Section C of the A. A. A. S. on "A Proposed Schedule of Allowable Differences and of Probable Limits of Accuracy in Quantitative Analyses of Metallurgical Materials."[1] The following quotation outlines the object and method of arriving at the values shown in Table I, which are taken from a longer table in the original paper:

> Many methods for the determination of the various elements usually met with in metallurgical work have been proposed, each having its own claim for accuracy, or rapidity, or both, but as will be seen from the efforts of the international committee on the analysis of iron and steel, we are far from having perfect methods for metallurgical analysis.
>
> There are many sources of error in ordinary quantitative determinations, which, while they can be partially avoided, can never be wholly overcome. Among these may be mentioned such errors as arise from solubility of precipitates, solubility of apparatus in which operations are performed, impurities in chemicals, inaccurate graduation of volumetric apparatus, unavoidable error in accuracy of weighing, and last, but not least, errors due to what may be termed the personal equation, the presence or absence in the operator of that manipulative skill which distinguishes an expert from a clumsy worker. Since we cannot expect absolute agreement in results, it may be asked how close should quantitative determinations agree? This question cannot be answered by a single figure, since the unavoidable errors in the various determinations differ according to the element determined and the method used in the analysis. Just how great a difference between determinations should be allowed and what the probable limit of accuracy which may be hoped for, is largely a matter of judgment based upon the examination of the results obtained by different chemists, known to be careful operators, working upon the same material.
>
> Basing our judgment upon the usual errors of analysis, upon the commercial requirements of accuracy and upon the unavoidable sources of error we would propose the following schedule of allowable differences and of probable limits of accuracy for discussion in the section. In the table below the first column shows the element or constituent determined; the second, a formula for calculating the difference which might be reasonably expected between the results of two chemists working upon the same material, and the third column shows a formula for calculating the probable minimum error which may be hoped for.

TABLE I

ELEMENT OR CONSTITUENT	Allowable Difference of Per cent	Probable Limit of Accuracy
	Iron and Steel	
Graphitic carbon..	± [0.050 + (0.02 × Cg)]	± [0.005 + (0.005 × Cg)]
Combined carbon in cast iron.....	± [0.050 + (0.02 × Cc)]	± [0.005 + (0.005 × Cc)]
Carbon in steel....	± [0.010 + (0.02 × C)]	± [0.002 + (0.003 × C)]
Silicon...........	± [0.005 + (0.02 × Si)]	± [0.002 + (0.003 × Si)]
Sulfur...........	± [0.003 + (0.03 × S)]	± [0.0005 + (0.005 × S)]
Phosphorus.......	± [0.002 + (0.02 × P)]	± [0.0002 + (0.005 × P)]
Manganese in cast iron and steel...	± [0.005 + (0.04 × Mn)]	± [0.001 + (0.005 × Mn)]
Nickel............	± [0.050 + (0.02 × Ni)]	± [0.005 + (0.005 × Ni)]
	Ores	
Silica............	± [0.050 + (0.006 × SiO_2)]	± [0.005 + (0.001 × SiO_2)]
Alumina.........	± [0.030 + (0.003 × Al_2O_3)]	± [0.005 + (0.001 × Al_2O_3)]
Iron.............	± [0.020 + (0.003 × Fe)]	± [0.004 + (0.001 × Fe)]
Manganese.......	± [0.050 + (0.003 × Mn)]	± [0.005 + (0.001 × Mn)]
Calcium oxide....	± [0.050 + (0.002 × CaO)]	± [0.010 + (0.001 × CaO)]
Magnesia.........	± [0.050 + (0.010 × MgO)]	± [0.005 + (0.002 × MgO)]
Phosphorus.......	± [0.002 + (0.02 × P)]	± [0.0002 + (0.005 × P)]
Phos. pentoxide...	± [0.005 + (0.02 × P_2O_5)]	± [0.0005 + (0.005 × P_2O_3)]

The object of the present paper is to bring out, by a comparison of variations computed from the table with those actually found by skilled observers working on the same sample, the desirability of some such formulas for comparing the work of different analysts, and to emphasize the fact that the proportionate variations in the determination of elements, especially those occurring in small quantities, are larger than is generally realized.

Undoubtedly the most valuable data for such a comparison are those given in the certificates of analyses issued by the Bureau

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[1] "International Standards for the Analysis of Iron and Steel," *Trans. Am. Inst. Mining Eng.*, October **1890**.

[1] *J. Am. Chem. Soc.*, **18** (1896), 35.

TABLE II—SILICON DETERMINATION IN CAST IRON

	Allowable Difference of Per cent ± [0.005 + (0.02 × Si)]		Individual Observers Maximum + and — Deviation from Certificate Value				Probable Limit of Accuracy ± [0.002 + (0.003 × Si)]		
B. of S. Sample	B. of S. Certificate Value	Allowable Difference Formula Applied	Method A Drown's Method	No. Observers	Method B Other Methods	No. Observers	Limit of Accuracy Formula Applied	Proportion Observers within Limit of Accuracy	Per cent within Limit of Accuracy
Iron B	1.267	±0.030	.. ..	.	+0.045 —0.032[1]	5	±0.006	1/5	20
Iron B 4*b*	1.34	±0.032	+0.06 —0.07	4	+0.03 —0.04[2]	7	±0.006	4/11	36
Iron B 4*a*	1.37	±0.032	+0.056 —0.044	11	.. ..	..	±0.006	5/11	45
Iron C	1.720	±0.039	.. ..	..	+0.040 —0.020[1]	5	±0.007	3/5	60
Iron C 5*a*	1.84	±0.042	+0.03 —0.03	11	.. ..	..	±0.008	4/11	36
Iron C 5*b*	1.84	±0.042	+0.04 —0.02	8	+0.04 —0.02[1]	5	±0.008	8/13	60
Iron C 5*c*	1.85	+0.042	+0.02 —0.03	4	+0.06 —0.06[2]	9	±0.008	2/13	15
Iron E	2.21	±0.049	+0.05 —0.03	7	+0.02 —0.03[1]	4	±0.009	6/11	55
Iron D 6*a*	2.57	±0.056	+0.05 —0.04	9	+0.06 0.08[1]	6	±0.010	6/15	40
Iron D 6*b*	2.59	+0.057	+0.06 —0.06	6	+0.04 —0.04[1]	5	±0.010	2/11	18
Iron D	2.64	+0.058	.. ..	..	+0.04 —0.03[1]	5	±0.010	1/5	20

[1] Method not stated

[2] HCl dehydration.

TABLE III—CARBON DETERMINATION IN STEEL

	Allowable Difference of Per cent ± [0.010 + (0.02 × C)]		Individual Observers Maximum + and — Deviation from Certificate Value				Probable Limit of Accuracy ± [0.002 + (0.003 × C)]		
B. of S. Sample	B. of S. Certificate Value	Allowable Difference Formula Applied	Method A Direct Combustion	No. Observers	Method B Solution and Combustion	No. Observers	Limit of Accuracy Formula Applied	Proportion Observers within Limit of Accuracy	Per cent within Limit of Accuracy
Bessemer 8*b*	..	...	... ...	..	... .	..	...	..	..
Bessemer 8*a*	0.084	±0.012	+0.003 —0.002	7	+0.007 —0.003	7	±0.002	8/14	57
Acid O. H. 0.1	0.103	±0.012	+0.003 —0.005	4	+0.021 —0.010	6	±0.002	3/10	30
Basic O. H. 15*a*	0.111	±0.012	+0.007 —0.003	6	+0.005 —0.007	6	±0.002	5/12	42
Bessemer 9*b*	0.184	±0.014	+0.015 —0.019	9	... ...	1	±0.003	1/ 9	11
Acid O. H. 19*a*	0.207	±0.014	+0.018 —0.010	9	+0.008 —0.012	4	±0.003	1/13	8
Acid O. H. 0.2	0.208	±0.014	+0.018 —0.007	4	+0.022 —0.017	6	±0.003	1/10	10
Basic O. H. 11*b*	0.211	±0.014	+0.014 —0.006	9	... ...	1	±0.003	7/ 9	77
Basic O. H. 11*a*	0.225	±0.014	+0.017 —0.003	6	+0.013 —0.017	6	±0.003	8/12	58
Basic O. H. 0.2	0.242	±0.015	+0.014 —0.013	3	+0.014 —0.015	8	±0.003	4/11	36
Bessemer 9*a*	0.254	±0.015	+0.006 —0.007	7	+0.006 —0.003	7	±0.003	10/14	71
Ni Steel 33	0.278	±0.016	+0.012 —0.012	7	+0.018 —0.010	4	±0.003	3/11	27
Cr-V Steel 30*a*	0.290	±0.016	+0.014 —0.016	10	... ...	..	±0.003	4/10	40
V Steel 24	0.350	±0.017	+0.024 —0.018	8	+0.009 —0.010	5	±0.003	3/13	23
Cr-Ni Steel 32	0.364	±0.017	+0.005 —0.003	6	+0.009 —0.009	7	±0.003	5/13	38
Basic O. H. 12*a*	0.372	±0.017	+0.015 —0.018	7	+0.010 —0.017	5	±0.003	5/12	42
Bessemer 10*b*	0.373	±0.017	+0.009 —0.015	8	+0.010 —0.006	7	±0.003	5/15	33
Cr-V Steel 30	0.373	±0.017	+0.013 —0.022	9	+0.010 —0.008	5	±0.003	3/14	21
Acid O. H. 0.4	0.377	±0.018	+0.012 —0.015	6	+0.013 —0.019	5	±0.003	2/11	18
Acid O. H. 20*a*	0.392	±0.018	+0.011 —0.013	9	... ...	1	±0.003	4/ 9	44
Basic O. H. 12*b*	0.409	±0.018	+0.005 —0.005	9	... ...	1	±0.003	6/ 9	67
Basic O. H. 0.4	0.436	±0.019	+0.021 —0.012	3	+0.023 —0.019	8	±0.003	3/11	27
Bessemer 0.4 Re	0.453	±0.019	+0.014 —0.021	6	+0.018 —0.014	6	±0.003	1/12	8
Bessemer 22*a*	0.578	±0.022	+0.011 —0.011	8	... ...	1	±0.004	1/ 8	13
Basic O. H. 13*a*	0.581	±0 022	+0.010 —0.012	7	+0.009 —0.017	6	±0.004	2/13	15
Acid O. H. 0.6	0.591	±0.022	+0.016 —0.009	6	+0.011 —0.010	6	±0.004	4/12	33
Bessemer 22	0.592	±0.022	+0.019 —0.018	9	+0.005 —0.010	3	±0.004	4/12	33
Cr-W Steel 31	0.599	±0.022	+0.011 —0.014	10	... ...	..	±0.004	6/10	60
Acid O. H. 21*a*	0.617	±0.022	+0.008 —0.016	9	... ...	1	±0.004	6/ 9	67
Bessemer 23	0.805	±0.026	+0.011 —0.015	9	+0.006 —0.004	3	±0.004	4/12	33
Basic O. H. 14*a*	0.815	±0.026	+0.011 —0.012	7	+0.005 —0.014	6	±0.004	7/13	56
Acid O. H. 34	0.84	±0.027	+0.01 —0.01	8	+0.01 —0.01	6	±0.005	2/14	14
Basic O. H. 16*a*	0.998	±0.030	+0.021 —0.017	8	+0.010 —0.007	5	±0.005	4/13	31
Acid O. H. 35	1.03	±0.031	+0.01 —0.02	7	+0.01 —0.02	5	±0.005	1/12	8
Basic O. H. 1.0	1.049	±0.031	+0.011 —0.014	4	+0.026 —0.018	9	±0.005	5/13	46

of Standards. Through the courtesy of the director of the Bureau, a complete set of these certificates has been received by this laboratory. These certificates extend from 1906 to 1919, inclusive, and may fairly be taken as representing the best practice during these years. All certificates, to the certificate value of which five or more observers contributed, and which were applicable to the above table, were included in the comparisons following.

In order to make these comparisons, itemized tables were made out for each element: six for the elements in cast iron; six for those in steel; and eight for iron and manganese ores. Each itemized table represents from 2 to 34 different samples, with not less than five observers reporting on each sample, while in six cases reports were submitted by more than 20 observers. The reason for the absence in the original table of formulas for computing elements so commonly found in alloy steels is easily seen in the date of publication, since at that time nickel steels were about the only ones in general use. From the itemized tables, summarized tables were made up, the method of computing the average values and deviations being similar to that used by the Bureau of Standards in computing certificate values, since the number of observers reporting each value was taken into consideration.

The descriptive heading of each itemized table shows the element determined and the formula for computing the allowable difference of per cent and the probable limit of accuracy. The different columns of the table represent: first, the Bureau of Standards sample with number; second, the certificate value; third, the allowable difference computed by applying the formula to the certificate value. The next four columns show the maximum + and — deviation from the certificate value with the number of observers reporting on each method, where more than one method was employed. In general, when more than one method was used, that which was most popular, as shown by the number of observers, is designated "A," while the next in number of observers is called "B." The eighth column shows the probable limit of accuracy computed by applying the formulas to the certificate value. The ninth column shows the fractional proportion of the total observers whose values come within the probable limit of accuracy, while the last column expresses this same value in per cent.

As silicon in cast iron and carbon in steel are two of the most frequent determinations required of steel-works chemists, the itemized tables (Tables II and III) for these two determinations are given as being typically representative of all.

In Table IV are shown the summarized results of these values. The first column shows the number of samples included in the itemized table from which the summarized values are computed. The second column gives the element determined, the third the range of certificate values in per cent, the fourth the average value, and the fifth the average allowable deviation computed by applying the formula to the average per cent. The next four columns show the averages of the maximum + and — deviations from the averages, together with the average number of observers by Methods A and B, as defined in describing the itemized tables. In the tenth column is given the average

TABLE IV—SUMMARIZED RESULTS FOR CAST IRON AND STEEL

No. Standards	Element Determined	Range of Certificate Values in Per cent	Mean Cert. Value	Allowable Difference Formula Applied to Cert. Value	Maximum + and — Deviations from Certificate Value						Limit of Accuracy Formula Applied to Mean	Proportion Observers within Limit of Accuracy	Per cent within Limit of Accuracy
					Method A		No. Observers	Method B		No. Observers			
					Cast Iron								
10	Graphite C...	1.79 –3.27	2.27	±0.10	+0.05	—0.07	8	...	...	..	±0.016	31/ 83	37
10	Combined C......	0.38 –0.67	0.55	±0.06	+0.05	—0.05	8	...	...	..	±0.008	27/ 82	33
11	Silicon...........	1.267–2.64	1.93	±0 04	+0.05	—0.04	7	+0.04	—0.04	6	±0.008	42/111	38
11	Sulfur...........	0.030–0.062	0.041	±0.004	+0.004	—0.004	9	+0.004	—0.004	6	±0.001	70/162	43
11	Phosphorus.......	0.092–0.862	0.331	±0.009	+0.010	—0.008	5	+0.006	—0.006	5	±0.002	37/ 98	38
11	Manganese... ...	0.444–1.54	0.945	±0.042	+0.016	—0.012	7	+0.013	—0.023	4	±0.006	58/ 98	59
					Steel								
34	Carbon..........	0.084–1.049	0.453	±0.019	+0.012	—0.013	7	+0.012	—0.012	6	±0.003	138/395	35
35	Silicon...........	0.003–0.303	0.120	±0.007	+0.006	—0.006	6	+0.007	—0.007	6	±0.002	154/369	42
35	Sulfur...........	0.019–0.103	0.045	±0.004	+0.003	—0 003	7	+0.004	—0.004	7	±0.001	244/485	50
35	Phosphorus.......	0.006–0.120	0.053	±0.003	+0.002	—0 003	5	+0.002	—0.003	4	±0.0005	122/301	40
35	Manganese.......	0.154–0.918	0.647	±0.030	+0.011	—0 011	7	+0.027	—0.024	6	±0.004	97/313	31
2	Nickel.....	1.62– 3.33	2.475	±0.100	+0.035	—0.025	9	...	...	..	±0.017	13/ 18	72

TABLE V—IRON AND MANGANESE ORES

B. of S. Sample	Determination	B. of S. Cert. Value	Allowable Difference Formula Applied	Individual Observers Maximum + and — Deviation from Certificate Value						Limit of Accuracy Formula Applied	Proportion Observers within Limit of Accuracy	Per cent of Observers within Limit of Accuracy
				Method A		No. Observers	Method B		No. Observers			
"Sibley" Iron Ore 27...	SiO_2	0.75	±0.10	+0.11	—0 07	21	..	..	..	±0.006	9/21	43
Magnetite Ore 29................	SiO_2	12.02	±0.12	+0.09	—0.06	5	..	..	..	±0.017	2/5	40
Crescent Iron Ore 2*b*.............	Al_2O_3	1.03	±0.03	+0.04	—0.03	9	+0.07	—0.03	17	±0.006	12/26	46
Magnetite Ore 29................	Fe	55.75	±0.19	+0.08	—0.10	6	..	..	..	±0.06	3/6	50
"Sibley" Iron Ore 27............	Fe	69.11	±0.23	+0.11	—0.26	9	+0.20	—0.18	19	±0.07	11/29	38
"Norrie" Iron Ore 28............	Mn	0.484	±0.05	+0.036	—0.044	24	..	..	..	±0.005	4/24	16
Manganese Ore 25................	Mn	56.36	±0.22	+0.09	—0.27	5	+0.27	—0.20	11	±0.06	4/16	25
Crescent Iron Ore 26............	CaO	2.64	±0.06	+0.26	—0.19	25	..	..	..	±0.013	1/25	4
Crescent Iron Ore 26............	MgO	3.44	±0.08	+0.32	—0.22	25	..	..	..	±0.011	2/25	8
"Sibley" Iron Ore 27............	P	0.037	±0.003	+0.004	—0.002	22	..	..	..	±0.0004	4/22	20
Magnetite Iron Ore 29...........	P_2O_5	1.01	±0.025	+0.01	—0.00	5	..	..	..	±0.0055	5/5	100

probable limit of accuracy computed by applying the formula to the average per cent. Column 11 gives in fractional proportion the number of all observers coming within the probable limit of accuracy, while in the twelfth column is shown the same value in per cent.

As comparatively few iron and manganese ores have been analyzed and certificates issued, the results of those determinations on which five or more observers have reported are given in Table V, which has been prepared by substantially the same system as that used to show the values for iron and steel.

A study of the results given in Table IV shows a very satisfactory agreement between the computed allowable deviation and that actually found by skilled workers in the case of the carbon, silicon, phosphorus, and sulfur, and the fact that considerably less than half of these experienced chemists come within the probable limit of accuracy bears out the original conclusion that insistence on agreement inside the computed limit of accuracy would be unreasonable. The close agreement of the deviations actually found with those computed is dependent on an allowable difference of more than two per cent of the element determined, a larger experimental difference than chemists usually realize.

The two exceptions, manganese and nickel, indicate very clearly the result of the improvements which have been made since 1895 in the methods for determining these two elements. The bismuthate method for manganese was first published in 1895, while the dimethylglyoxime method for nickel is of much more recent origin.

In view of the largely increased number of elements which metallurgical chemists are called upon to determine, there seems to be need of a schedule somewhat similar to that given in Table I for computing allowable differences and probable limits of accuracy, but extended to take in all the elements determined, the formula being modified where necessary to bring the results in close accord with the best modern practice. If such a revised schedule were prepared under the supervision of the Bureau of Standards, and issued with the certificates accompanying the analyzed samples sent out, it would be of much service to chemists in checking up the accuracy of their own work and in interpreting chemical specifications.

SCIENTIFIC SOCIETIES

SIXTIETH MEETING AMERICAN CHEMICAL SOCIETY, CHICAGO, ILL., SEPTEMBER 6 TO 10, 1920

PROGRAM OF PAPERS

GENERAL SESSIONS

Julius Stieglitz, Honorary Chairman. Address of Welcome.

Joseph R. Noel, President of the Noel State Bank and Vice President, Chicago Association of Commerce. Address of Welcome.

W. A. Noyes, President, American Chemical Society. Response.

Thomas E. Wilson, President, Wilson & Co. The Value of Technical Training in the Reconstruction of Industries.

A. S. Loevenhart, Head of Department of Pharmacology of the University of Wisconsin. Chemistry's Contribution to the Life Sciences.

H. P. Talbot. Relation of Educational Institutions to the Industries.

W. A. Patrick. Some Uses of Silica Gels.

W. A. Noyes. President's Address—Chemical Publications.

AGRICULTURAL AND FOOD CHEMISTRY DIVISION

C. E. Coates, *Chairman* T. J. Bryan, *Secretary*

1. **Edward Gudeman.** Antitoxins as Food Preservatives.
2. **Melvin De Groote.** The Solubilities of Vanillin and Coumarin in Glycerol Solutions.
3. **Henry A. Schuette and M. Josephine Prichett.** A Study of the Determination of Fat in Casein.
4. **R. H. Carr.** Do Greens Aid the Growth of Chicks in Confinement?
5. **C. H. Bailey.** The Hydroscopic Moisture of Flour Exposed to Atmospheres of Different Humidities.
6. **F. C. Cook.** The Composition of the Tubers, Skins, and Sprouts of Three Varieties of Potatoes.
7. **F. C. Cook.** Pickering Bordeaux Sprays.
8. **William Brinsmaid.** A Test for Annatto in Fats and Oils. (By title)

BIOLOGICAL CHEMISTRY DIVISION

R. A. Gortner, *Chairman* A. W. Dox, *Secretary*

1. **Howard B. Lewis and Genevieve Stearns** Diet and Sex as Factors in Creatinuria in Man.
2. **Carl O. Johns and A. J. Finks.** Nutritive Value of the Proteins of Tomato Seed Press Cake. (Lantern.)
3. **D. B. Jones and Carl O. Johns.** Hydrolysis of the Globulin of the Coconut, *Cocos nucifera*. (Lantern.)
4. **Carl O. Johns and Chas. E. F. Gersdorff** The Globulin of the Cohune Nut, *Attalea cohune*. (Lantern.)
5. **Carl O. Johns and Henry C. Waterman.** Some Proteins of the Mung Bean, *Phaseolus aureus*. (Lantern.)

6. J. S. Hughes. The Effect of the Fat-soluble Vitamine Content of a Feed on the Fat-soluble Vitamine Content of Adipose Tissue. (Lantern.)
7. Arthur D. Hirschfelder, M. C. Hart and F. J Kucera. The Local Anesthetic and Antiseptic Applications of Saligenin and Its Derivatives and Allied Compounds.
8. H. C. Gore. Occurrence of Diastase in the Sweet Potato in Relation to the Preparation of Sweet Potato Sirup.
9. A. D. Emmett. Polyneuritis as Influenced by the Amount of Protein and Carbohydrate Present.
10. A. R. Lamb. The Acid-Base Balance in Animal Nutrition. IV—The Tolerance of Rabbits to Acid Rations over Long Periods of Time.
11. V. E. Nelson and A. R. Lamb. Further Studies on the Effect of Fat-soluble Vitamine Deficiency.
12. J. F. McClendon. The Hydrogen-Ion Concentration of the Contents of the Small Intestine.
13. S. L. Jodidi, S. C. Moulton and K. S. Markley. A Mosaic Disease of Cabbage as Revealed by Its Nitrogen Constituents.
14. R. Adams Dutcher, Cornelia Kennedy and C. H. Eckles. The Influence of the Diet of the Cow upon the Fat-soluble and Water-soluble Vitamine of Cow's Milk.
15. R. Adams Dutcher, C. H. Eckles, C. D. Dahle, S. W. Mead and O. G. Schaefer. The Influence of the Diet of the Cow upon the Antiscorbutic and Nutritive Properties of Cow's Milk.
16. R. Adams Dutcher and S. D. Wilkins. The Influence of the Diet upon the Growth and Development of Testes and Adrenals in White Leghorn Cockerels.
17. R. Adams Dutcher, Geo. E. Holm and Harlow Bierman. Further Observations of the Antineuritic Properties of Chemical Substances.
18. Paul Francis Sharp and Ross Aiken Gortner. A Study of Certain Physicochemical and Colloidal Properties of the Glutens from Strong and Weak Flours.
19. C. H. Bailey and S. D. Wilkins. Further Observations on the Relation between the Imbibition of the Gluten and the Strength of Wheat Flour.
20. Geo. E. Holm and Walter F. Hoffman. Some Observations on the Isolation of Cystine from Keratin.
21. J. J. Willamann and M. Sandstrom. Biochemistry of Plant Diseases. III—Effect of the Brown Rot Organism on Plums.
22. Edgar J. Witzemann. The Apparently Specific Effect of Ammonia on the Oxidation of Butyric Acid with Hydrogen Peroxide.
23. F. M. Huntoon, Peter Masucci and E. Hannum. Antibody Studies. III—A Preliminary Report on the Chemical Nature of Bacterial Antibodies.
24. Sergius Morgulis and Victor E. Levine. The Non-catalase Decomposition of Hydrogen Peroxide by Aromatic Hydrocarbons and Their Derivatives.
25. Sergius Morgulis and Victor E. Levine. The Dynamics of the Catalase Reaction.
26. Victor E. Levine. The Action of Proteins on the Phenol Reagent of Folin and Dennis.
27. C. F. Langworthy and H. J. Deuel. Digestibility of Some Raw Starches.
28. Pauline M. Avery, R. R. Mellon and S F. Acree. Uses in Biological Sciences for Standardized Sterile Buffer Tablets and for a Single Sterile Buffer Solution Covering All P*h* Values.
29. Pauline M. Avery, R. R. Mellon and S. F. Acree. On the Ionization Constant of Glycerophosphoric Acid and the Use of Carbohydrate Phosphate as Buffers and Nutrients, Especially in Culture Media.
30. J H. Hopfield, J. B. Halstead, Marguerite A Brennan and S. F. Acree. Hydrogen Electrode Measurements of the Acid and Basic Ionization Constants of Asparaginic Acid and Its Value as a Buffer and Nutrient Material in Culture Media.
31. A. W. Homberger and B. Mathin. The Nitrogenous Constituents of Condensed Milk as Compared with Fresh Milk.
32. Chi Che Wang and Mamie Dentler. The Creatinine and the Creatine of the Blood of Normal Women.
33. Harper F. Zoller. The Buoying Up of the Equilibrium of Milk Salts during Heat Treatment.
34. Harper F. Zoller Hydrogen-Electrode Study of the Curdling in Casein Solution at High Temperature.
35. H. C. Hamilton. Chemistry of Digitalis.

DYE CHEMISTRY DIVISION

Charles L Reese, *Chairman* R. Norris Shreve, *Secretary*

1. A. S. Wheeler. New Naphthalene Dyes.
2. J. H Carpenter. Applications of Maleic and Fumaric Acids and their Salts to the Textile Industry.
3. E. R. Brunskill. The Anilides of β-Oxynaphthoic Acid.
4. R. E. Rose. The Education of the Research Chemist.
5. Harry McCormack. Extraction of Resorcinol from the Alkali Melt.
6. Louis E. Wise. Photosensitizing Dyes. (Lantern.)
7. Louis A. Mikeska. The Preparation of Lepidine and Related Bases. (Lantern.)
8. E. Q Adams and Herbert L. Haller. Isocyanine Dyes from Lepidine and Its Homologs. (Lantern.)
9. E. Q. Adams and H. L. Haller. Kryptocyanines: A New Series of Photosensitizing Dyes. (Lantern).
10. Louis A. Mikeska, Herbert L. Haller and Elliot Q. Adams. Synthesis of Photosensitizing Dyes. II—Dicyanine. (Lantern.)
11. Joseph A. Ambler. Naphthalene Sulfonic Acids. III—An Alternative Method for the Qualitative Detection of Naphthalene-2,7- and 1,6-Disulfonic Acids. (Lantern.)
12. D. F. J. Lynch. Substituted Naphthalene Sulfonic Acids. I. (Lantern.)
13. C. E. Senseman. Benzene Disulfonic Acid from Benzene Monosulfonic Acid. (Lantern.)
14. M. L. Crossley. Qualifications of Organic Chemists.
15. C. B. Ogilvie, G. S. Simpson and M. L. Crossley. Standard Laboratory Equipment.
16. M. L. Crossley. Actions of Sulfuric Acid on Nitro Carbocyclic Compounds.

FERTILIZER DIVISION

F. B. Carpenter, *Chairman* H. C. Moore, *Secretary*

I—Papers

1. J W. Turrentine. Kelp as a Basis of an American Potash Industry.
2. C. H MacDowell. Relationships of Chemistry and the Fertilizer Industry.
3. E. G. Proulx. A Perfect Fertilizer Law.
4. J. E. Breckenridge. Boron in Relation of the Fertilizer Industry.
5. J. M. Bartlett. The Quantitative Estimation of Borax in Mixed Fertilizers.
6. F. B Carpenter. Note on the Determination of Nitrogen in Fertilizers Containing Both Organic and Nitric Nitrogen.
7. Rolla N. Harger. Dicyanodiamide. A Rapid Direct Method for Its Determination in Cyanamid and Mixed Fertilizers.
8. Rolla N. Harger The Changes Taking Place in Cyanamid when Used in Mixed Fertilizers.
9. R. D. Caldwell and H. C. Moore. Some Results of Determination of Potash by the Lindo-Gladding Method Using Alcohol of Various Strengths in the Presence of Sodium Salts.
10. F. B. Carpenter. Injurious Effects of Borax on Field Crops.
11. B. F. Robertson. The "Blank" in the Kjeldahl Process: Its Analytical and Commercial Significance.
12. M. M. Austin and S. W. Parr. Potash Shales of Illinois.
13. H. A. Huston. Potash Situation in Germany.

II—Reports of Committees

1. Sampling. F. S. Lodge, *Chairman.*
2. Fertilizer Legislation. J. E. Breckenridge, *Chairman.*
3. Research and Analytical Methods. Paul Rudnick, *Chairman*

INDUSTRIAL AND ENGINEERING CHEMISTRY DIVISION

H. D. Batchelor, *Chairman* H. E. Howe, *Secretary*

I—Symposium on Cellulose Chemistry

1. Chas. Baskerville and Clarence M. Joyce. Regenerating Book Stock.
2. Chas. Baskerville and Reston Stevenson. Recovering News Print.
3. Louis Kahlenberg Cellulose Content of Various Compound Celluloses.
4. Harold Hibbert. The Constitution of Cellulose.
5. E. C. Sherrard and G. W. Blanco. Acid Hydrolysis of Sugar-cane Fiber and Cottonseed Hulls.
6. E. C Sherrard and G W. Blanco. The Preparation and Analysis of a Cattle Food Consisting of Hydrolyzed Sawdust.
7. S. A. Mahood and D. E. Cable. A Comparison of Wood Cellulose and Cotton Cellulose.
8. Hugh P. Baker. Supply and Preparation of Wood for the Manufacture of Pulp.
9. J. E. Minor. Parchmentizing Paper and the Reaction of Mordants.
10. G. J. Esselen, Jr Is It Feasible to Form a Section of Cellulose Chemistry?

II—Papers

11. Chas. Baskerville. Solvents for Phosgene.
12. Edward G. Mahin and R. E. Brewer. Electrometric Method for Detecting Segregation of Dissolved Impurities in Steel. (Lantern.)
13. Robt. E. Wilson. Soda Lime for Industrial Purposes. (Lantern.)
14. Robt. E. Wilson and M. Seltzer Flow of Viscous Liquids through Pipes. (Lantern.)
15. H. K. Benson and A. L. Bennett. New Solvents for Rosin Extraction.
16. H. C. Howard. Comparative Study of Vibration Absorbers.
17. Hugo Schlatter. Catalysis in the Manufacture of Ether.
18. Harold Van Doren and James R. Withrow. Use of Platinum Crucibles in Electro-analysis. Copper Determination.
19. Rufus D. Reed and James R. Withrow. Use of Platinum Crucibles in Electro-analysis. Rapid Copper Determination.

20. H. McCormack. Estimation of Benzene in Admixture with Paraffin Hydrocarbons.
21. H. McCormack. Preparation of Manganates and Permanganates.
22. H. S. Coith and James R. Withrow. Permanganate Determination of Sulfur Dioxide.
23. F. C. Vilbrandt, Samuel L. Shenefield and James R. Withrow. Action of Permanganate upon Sulfur Dioxide and Sulfides.
24. Gordon D. Patterson and James R. Withrow. Iodimetric Determination of Sulfur Dioxide.
25. W. D. Collins. Uniform Packages for Reagent Chemicals.
26. R. M. Wilhelm. Uniform Specifications for Chemical Thermometers.
27. O. L. Barnebey. Recovery of Industrial Gases with Activated Charcoal.
28. H. V. Main. A Comfortable Dust Respirator.
29. O. R. Sweeney and Joseph Ellert. Evidences of Autocatalysis in the Hydrogenation of Cottonseed Oil.
30. Charles L. Parsons. The Use of Ammonia Oxidation *versus* Niter in Chamber Acid Production.
31. Harrison Hale and G. O. Burr. Separation of Iron from Aluminium by Precipitation as Prussian Blue. (By title.)

III—Fuel Symposium

32. S. W. Parr. Low Temperature Carbonization and Its Application to High Oxygen Coals.
33. Edgar Stansfield. Carbonization of Canadian Lignite.
34. Henry Kriesinger. By-product Coke, Anthracite, and Pittsburgh Coal as Fuel for Heating Houses.
35. F. W. Sperr, Jr. By-product Coking.
36. G. A. Burrell, G. G. Oberfell and C. L. Voress. The Charcoal Method of Gasoline Recovery.
37. S. E. Sheppard. Colloidal Fuels. Their Preparation and Properties.
38. A. C. Fieldner, G. W. Jones and A. A. Straub. Gasoline Losses Due to Incomplete Combustion in Motor Vehicles.
39. J. B. Garner. Enrichment of Artificial Gas with Natural Gas.
40. Harry A. Curtis. Commercial Realization of Low-Temperature Carbonization of Coal.
41. Horace C. Porter. Fuel Conservation, Present and Future.
42. Alfred R. Powell. Some Factors Affecting the Sulfur Content of Coke and Gas in the Carbonization of Coal.
43. H. F. Yancey and Thomas Fraser. Distribution of the Forms of Sulfur in the Coal Bed. (Lantern.)

LEATHER CHEMISTRY SECTION

E. E. Marbaker, *Chairman* William Klaber, *Secretary*

1. John Arthur Wilson and Erwin J. Kern. Nature of the Hide-Tannin Compound and Its Bearing upon Tannin Analysis.
2. John Arthur Wilson. The Mechanism of Bating.
3. F. C. Orthmann. Chemical Control of the Tannery.
4. V. H. Kadish. A New Method for the Recovery of Nitrogenous Fertilizer Material from Tannery Waste Sulfide Liquors.
5. Alan A. Claflin. The Influence of Acids on the Tannin Content of Tan Liquors.
6. G. D. McLaughlin and R. E. Porter. The Swelling and Falling of White Hide in Vegetable Tan Liquors.
7. P. R. Roberts. Dyes as Used in the Leather Trade.
8. A. W. Thomas and Margaret W. Kelley. The Effect of Concentration of Chrome Liquors in the Adsorption of Its Constituents by Hide Substance.
9. A. W. Thomas and A. Frieden. The Determination of Hydrochloric Acid and Chlorides in Leather.
10. A. W. Thomas. Comment on Wilson and Kern's Recent Contribution to the Knowledge of Vegetable Tanning Agents.

ORGANIC CHEMISTRY DIVISION

E. Emmet Reid, *Chairman* Roger Adams, *Secretary*

1. W. L. Evans, J. E. Day and W. R. Stemen. The Oxidation of Propylene Glycol by Means of Alkaline Potassium Permanganate.
2. W. L. Evans and Lily Bell Sefton. The Oxidation of Isopropyl Alcohol and Acetone by Means of Alkaline Potassium Permanganate.
3. W. L. Evans and C. D. Looker. The Influence of Alkali on the Formation of Vinyl Alcohol from Acetaldehyde.
4. Thomas G. Thompson and Henry Odeen. The Solubility of Dichlorodiethyl Sulfide in Petroleum Hydrocarbons and Its Purification by Extraction with These Solvents.
5. Oliver Kamm and M. E. Dreyfus. Rearrangement of Unsaturated Acids.
6. Oliver Kamm and W. F. Day. The Reaction Velocity of Dealkylation of Tertiary Amines with Acyl Halides.
7. Rufus M. Kamm. The Alcoholysis of Esters with Amino Alcohols.
8. Roger Adams and Charles Shattuck Palmer. Reactions of the Arsines. Condensation of Primary Arsines with Aldehydes.
9. Ben. H. Nicolet. The Non-identity of Eleostearic Acid from Tung Oil with Ordinary Linolic Acid.
10. Ben. H. Nicolet and Imogene H. Willard. A New Type of Nitrogen-Sulfur Compounds; the Action of Chloramine-T on Alkyl Sulfides.
11. Hans T. Clarke. Report on the Progress of the Manufacture of Research Organic Chemicals.
12. Robert E. Wilson and Everett W. Fuller. The Production of Benzoic Acid and Benzophenone from Benzene and Phosgene.
13. Carleton E. Curran and C. E. Boord. The Nature of the Reactions of Anilines upon Nitrosophenol.
14. Chas. Raiford. Reduction of Polynitrophenols by Hydrogen Sulfide in the Presence of Ammonia.
15. F. B. Dains and E. Wertheim. The Action of Ammonia and Substituted Amines on Allophanic Ester.
16. H. L. Lochte and J. R. Bailey. Hydrazoisopropane.
17. J. B. Conant and E. L. Jackson. A Convenient Method for Preparing Certain Bromohydrins.
18. J. B. Conant. Addition Reactions Involving an Increase in Valence of a Single Atom.
19. D. S. L. Sherk and Edward Kremers. New Derivations of Thymol and Carvacrol.
20. Nellie A. Wakeman and Harlan G. Groffman. The Action of Amines upon Thymoquinone.
21. Frank C. Whitmore and E. B. Middleton. Organic Mercury Compounds of Phenol.

PHARMACEUTICAL CHEMISTRY DIVISION

Charles E. Caspari, *Chairman* Edgar B. Carter, *Secretary*

I—Papers

1. C. S. Leonard and Edward Kremers. A New Organic Arsenical and Related Compounds.
2. L. E. Sayre. Available Chlorine for Disinfectant Bath.
3. Chas. Baskerville and Myron Hirsch. Rate of Evaporation of Ethyl Chloride from Oils.
4. Chas. Baskerville. Experiences with and New Applications of Oil-Ether in Anesthesia.
5. E. H. Volwiler. Some Recent Anesthetics.
6. Hugh A. McGuigan. The Origin and Biological Significance of the Diastases.
7. H. A. Shonle and P. Q. Row. New Benzyl Esters Possessing Antispasmodic Action.
8. Mortimer Bye. Benzyl Succinate.
9. E. A. Wildman. Benzyl Derivatives of Salicylic Acid.
10. H. W. Rhodehamel and E. H. Stuart. Atropine Sulfate from *Datura stramonium*.
11. H. W. Rhodehamel and E. H. Stuart. Some New Compounds of Phenylcinchoninic Acid.
12. A. E. Stearn, H. V. Farr and N. P. Knowlton. An Investigation of the U. S. P. Assay of Phosphoric Acid and Soluble Phosphates.
13. S. A. Mahood. The Production of American Storax from the Red Gum Tree.

II—Symposium

The National Research Council and the Chemistry of Medicinal Products. A general discussion led by J. M. Francis on the possibilities to be found in the realm of the chemistry of medicinal products which may well be touched upon by the efforts of the National Research Council. The following members have been invited to participate in the symposium: Wilder D. Bancroft, Julius Stieglitz, Carl L. Alsberg, Chas. H. Herty, Frank R. Eldred, Chas. E. Caspari, H. V. Arny, and J. P. Snyder.

PHYSICAL AND INORGANIC CHEMISTRY

Wm. D. Harkins, *Chairman* H. N. Holmes, *Secretary*

1. W. J. Bently and Paul L. Stern. Preparation of Zinc Nitride.
2. H. V. Tarter. Hydrolysis of the Calcium Phosphates.
3. R. H. Bogue. On the Hydrolysis of the Silicates of Sodium.
4. H. H. Willard and R. K. McAlpine. A Revision of the Atomic Weight of Antimony. Final Report on the Analysis of the Tribromide.
5. Louis Kahlenberg. On the Separation of Crystalloids from One Another by Dialysis.
6. S. E. Sheppard, Felix A. Elliott, Harry D. Gideonse and (Miss) C. M. Godden. Investigations on Gelatins. Decay of Viscosity on Hydrolysis as a Function of Hydrogen-Ion Concentration.
7. (Miss) A. J. Benedict and Felix A. Elliott. Investigations on Gelatins. Protein Errors of Indicators.
8. Harry N. Holmes and W. C. Child. Gelatin as an Emulsifying Agent.
9. Harry B. Weiser and Edmund B. Middleton. Adsorption of Precipitates. III—The Adsorption of Precipitating Ions by Hydrous Aluminium Oxide.
10. Farrington Daniels and Elmer Johnston. The Thermal Decomposition of Gaseous Nitrogen Pentoxide: A Monomolecular Reaction. (Lantern.)
11. S. A. Braley and R. F. Schneider. The Structure of Gold Amalgams. (Lantern.)
12. Robert E. Wilson. Some New Methods for Determining the Vapor Pressure of Hydrated Salts. (Lantern.)

13. Alan W. C. Menzies. Measuring Low Vapor Pressures.
14. H. S. Taylor and A. W. Gauger. Adsorption of Gases by Nickel Catalyst and the Mechanism of Hydrogenation.
15. Felix A. Elliott and S. F. Acree. A New Form of Titration Hydrogen Electrode.
16. W. S. Hendrixson. Electrometric Standardizing of Potassium Dichromate with Hydriodic Acid and the Asserted "Super-oxidizing Value" of the Former.
17. W. D. Harkins. The Isotopes of Lithium as Related to the Constitution of the Nuclei of Atoms. (Lantern.)
18. Arthur E. Hill. The Distribution of Strong Electrolytes between Benzene and Water.
19. A. F. O. Germann and H. S. Booth I—The Cryoscopy of Boron Trifluoride Solutions: System with Hydrogen Sulfide.
20. James E. Wildish. The Dielectric Constant of Selenium Oxychloride.
21. D. A. McInnes. Ion Conductance of Strong Electrolytes.
22. Elliot Q. Adams. The Independent Origin of Acrinium.
23. Lloyd K. Riggs and C. Walter Eberlein. Nephelometric Estimation of Sulfur and Barium.
24. J. M. Bell, E. B. Cordon, F. H. Spry and W. White. Further Studies on the Freezing Points of the Nitrotoluenes.
25. Arthur E. Hill. The System Water-Benzene-Silver Perchlorate.
26. A. F. O. Germann and Vernon Jersey. II—The Cryoscopy of Boron Trifluoride Solutions: System with Phosgene. (Lantern.)
27. A. F. O Germann and Wendell Phillips. III—The Cryoscopy of Boron Trifluoride Solutions: Systems with Sulfur Dioxide and with Nitric Oxide. (Lantern.)
28. A. F. O. Germann and Leland R. Smith. IV—The Cryoscopy of Boron Trifluoride Solutions: System with Hydrogen Chloride. (Lantern.)
29. Felix A. Elliott and S. F. Acree. Conductance Corrections and Ionic Mobilities from Hydrated-Ion Concentration Measurements.
30. (Miss) A. D. Dushak, Felix A. Elliott and S. F. Acree. Contact Potentials in Hydrogen-Ion Determinations.
31. (Miss) A. D. Dushak, Felix A. Elliott and S. F. Acree. Titration Curves of Some New Buffer Mixtures.
32. S. E. Sheppard and Felix A. Elliott. Investigations on Gelatins: The Gold Number.
33. H. S. Taylor and G. Dougherty. The Hydrogenation of Benzene.
34. Nathaniel H. Furman and Alan W. C. Menzies. Period of Induction Preceding Changes of Hydration in the Hydrates of Cupric Sulfate.
35. Alan W. C. Menzies. Certain Physical Properties of Three Oils.
36. Harry B. Weiser and Allen Garrison. The Oxidation and Luminescence of Phosphorus. I—The Behavior of Phosphorus in Pure Oxygen.
37. Farrington Daniels and Elmer Johnston. The Photochemical Decomposition of Gaseous Nitrogen Pentoxide. (Lantern.)
38. Henry C. Waterman and Curtis M. Parkhurst. An Improved Method for the Preparation of Cuprous Chloride and Cuprous Bromide. (By title.)
39. Irving Langmuir. Radiation as Factor in Chemical Action.
40. D. M. Dennison and Irving Langmuir. The Crystal Structure of Ice.

RUBBER DIVISION

W. K. Lewis, *Chairman* Arnold H. Smith, *Secretary*

1. Reports.
2. Discussion: Shall the Rubber Division Publish an Annual Volume of Reprints and Lengthy Abstracts of Everything of Interest to the Rubber Chemist Made Public during the Year?
3. Election of Officers.
4. W. B. Wiegand. Rubber Energy. (Lantern.)
5. New Jersey Zinc Co. Research Laboratories. The Aging of Some Rubber Compounds. (Lantern.)
6. New Jersey Zinc Co. Research Laboratories. Some Microsections Cut from Vulcanized Rubber Articles. (Lantern.)
7. G. D. Kratz, A. H. Flower and B. J. Shapiro. II—The Action of Certain Organic Accelerators in the Vulcanization of Rubber.
8. G. D. Kratz, A. H. Flower and B. J. Shapiro. III The Action of Certain Organic Accelerators in the Vulcanization of Rubber.
9. J. F. Schufter. Method for the Determination of Free Sulfur and Antimony Tri- and Pentasulfides in Golden Antimony.
10. J. B Tuttle. The Action of Heat and Light on Vulcanized Rubber.
11. C. W. Bedford and Winfield Scott. A Theory of Acceleration Based on the Formation of Polysulfides during Vulcanization.
12. Symposium: The Analysis of Rubber, led by W. W. Evans. There will be discussions of various topics by H. L. Fisher, A. H. Smith, J B. Tuttle, H. E. Simmons, C. W. Sanderson, W. W. Harrison, H. B. Underwood, C. R. Boggs, P. A. Ritter, and others.
13. Round Table Discussion of Recent Developments. There will be samples on exhibit of rubber vulcanized by Peachey's nascent sulfur method

SUGAR CHEMISTRY DIVISION

C. A. Browne, *Chairman* Fred J Bates, *Secretary*

1. Chas. A. Gamble. The Sugar Industry of Peru.
2. G. L. Spencer. Electric Oven for Rapid Moisture Tests.
3. C. E Coates. Refining Raw Sugars without Bone-black.
4. W. D. Horne. Recent Advances in Defecation.
5. Frederick Bates and Associates. Comparative Analyses of Refined Sugars.
6. C. A. Browne. Graphic Method for Estimating Reducing Sugars in the Presence of Sucrose.
7. W. B. Newkirk and C. F. Snyder. Commercial Production of *d*-Mannite.
8. G. L. Spencer. The Preservation of Bagasse in Sugar Cane Mill Control.
9. M. J. Proffitt Glass Vacuum Pan for Laboratory Use.
10. A F. Blake. Changes in the Polarizing Constants of Sugars during Refining.
11. T. H. Murphy. Report on the Sugar Industry of France since the War. (Lantern.)
12. R. F. Jackson and C. L. Gillis. The Composition and Preparation of a Sugar Sirup of Maximum Solubility.
13. C. A. Browne. Some Characteristics of Imported Cane Sugars.
14. Edmond H. Eitel. American Progress in Bacteriological Sugars.
15. Longfield Smith. Results of Sugar Cane Experiments in St. Croix.
16. H. S. Paine and C. F. Walton, Jr. Use of Kieselguhr in the Clarification of Cane Juice.
17. W. B. Newkirk. Determination of the Density of Molasses.
18. R F. Jackson and C. L. Gillis. Determination of Sucrose and True Raffinose in Beet Products.

WATER, SEWAGE AND SANITATION DIVISION

J. W. Ellms, *Chairman* W. W. Skinner, *Secretary*

1. A. S. Behrman. Water Softening for the Manufacture of Raw Water Ice.
2. Harry E. Jordan Specifications for Glassware for Waterworks Laboratories.
3. W D. Collins. Hardness of Surface Waters in the United States.
4. Edward Bartow. The New Sewage Testing Station of the Illinois State Water Survey Division.

THE CHEMICAL SOCIETIES IN NEW YORK CITY

1920-1921 SEASON—RUMFORD HALL, THE CHEMISTS' CLUB

October 1—Société de Chimie Industrielle.
October 8—Society of Chemical Industry. *Joint Meeting* with Société de Chimie Industrielle.
October 22—American Chemical Society. *Joint Meeting* with Société de Chimie Industrielle.
November 5—Society of Chemical Industry.
November 19—American Chemical Society.
December 10—American Chemical Society. *Joint Meeting* with Society of Chemical Industry, American Electrochemical Society, and Société de Chimie Industrielle.
January 7—American Chemical Society.
January 14—Society of Chemical Industry. *Perkin Medal Award.*
February 11—American Electrochemical Society. *Joint Meeting* with Society of Chemical Industry, American Chemical Society, and Société de Chimie Industrielle.
March 11—American Chemical Society. *Nichols Medal Award.*
March 25—Society of Chemical Industry.
April 22—Society of Chemical Industry. *Joint Meeting* with American Electrochemical Society, Société de Chimie Industrielle, and American Chemical Society.
May 6—American Chemical Society.
May 13—Société de Chimie Industrielle. *Joint Meeting* with American Chemical Society, Society of Chemical Industry, and American Electrochemical Society.
May 20—Society of Chemical Industry.
June 10—American Chemical Society.

NOTES AND CORRESPONDENCE

BETTER CHEMICAL NOMENCLATURE IN TRADE USAGE

Significant and very encouraging for the general use of better chemical nomenclature and orthography in America is the recent action of E. I. du Pont de Nemours & Co. in adopting names and spellings for its dyestuff intermediates which correspond with the usage considered best from a scientific point of view. The improved names are to be used by the Sales and Advertising Department and their use is being urged on others. Trade journals are showing a willingness to adopt these names, and every indication seems to be that the movement will assume a national aspect. In the past the greatest obstacle to the needed improvement in chemical nomenclature in this country has been the slowness of manufacturers of, and dealers in, chemical substances to change over to better names and spellings (better English, correct endings to designate class, etc.) from the frequently unsatisfactory ones which came into use in the early days when German business and influence were preponderant in our chemical trade. This has perhaps been natural enough but none the less unfortunate. The ice has been broken now, and it is to be hoped that the old reluctance to make changes will disappear. The dyestuff field is not the only one in which reform is needed.

The greatest appeal to the trade will very likely be from the point of view of standardization. There is a diversity of names and particularly of spellings in the case of many chemical substances. Accuracy and convenience will be promoted by the adoption and use of one name and spelling as a standard in each case. To avoid a new and added source of confusion caution is of course necessary in the establishment of standard forms. Standards cannot be multiplied. The American Dyes Institute has been suggested as the proper authority for the standardization of the names of compounds of interest to the dye industry. This institute or any other organization interested in chemical names will no doubt be willing to coöperate with the Committee of the American Chemical Society on Nomenclature, Spelling and Pronunciation, which committee in turn is coöperating with similar committees of the British chemical societies. Our committee is progressing, slowly of necessity, in the adoption of rules and forms, and I am sure that I can say for the committee that we will be glad to do all that we can to aid in the establishment of better usage in the trade. Such a movement has been on our program for a little later when further advanced in our work.

E. J. Crane, *Chairman*,
Committee on Nomenclature, Spelling
and Pronunciation

Columbus, Ohio
July 30, 1920

CHEMICAL READING COURSES

Editor of the Journal of Industrial and Engineering Chemistry:

In connection with the "Chemical Reading Courses" appearing in the July and August 1920 issues of the Journal, the attention of small libraries and general readers might profitably be called to two points not specifically mentioned, but, unfortunately, not always obvious to the layman who has an authoritative list at hand:

1—The constant output of new books makes it desirable to consider, also, the very latest literature for possible material supplementing the "Courses."

2—Since the "Courses" are brief lists selected from a large mass of literature, librarians should keep in mind the fact that there are available many other general works, and many works too special to be included, some of which may be of particular value in special cases.

Applying these suggestions to a single field—ferrous metallurgy—we find that "Electric Furnaces in the Iron and Steel Industry," by Rodenhauser *and others*, is available in a later edition than that mentioned.

Among the books *not* mentioned, "The Making, Shaping and Treating of Steel," by J. M. Camp and C. B. Francis, has appeared in a second edition (the first, published in 1919, was not widely distributed). It affords the best existing guide to modern American practice in iron and steel manufacture. "Iron and Steel," by H. P. Tiemann, is a dependable, encyclopedic guide to obsolete as well as modern processes. It is comprehensive in scope and, for the average library, it will furnish concise answers to more questions than will any other single work on ferrous metallurgy. La Verne W. Spring's "Non-technical Chats on Iron and Steel and Their Application to Modern Industry" is a popular, descriptive work of high value to the general reader.

The three books mentioned in the preceding paragraph are general in scope and the average library will find it advantageous to purchase them in addition to, *or instead of*, the works mentioned in the "Chemical Reading Courses." Specific problems, calling for books of a more special nature, will vary with each community and unlimited inclusion of such books is, of course, beyond the scope of these "Courses," but it is well to bear in mind that excellent American works are available, also, on many of the more specific problems of the iron and steel industry; for example, chemical analysis.

The "Chemical Reading Courses" are apparently not primarily intended to suggest reference literature, but perhaps a dozen of the titles listed are distinctively reference works. Since a beginning has been made, it might not be amiss to suggest to librarians the advisability of consulting some of the up-to-date reference lists, such as "Chemical Literature and Its Use," by Marion E. Sparks, 1919, and "Some Observations on Chemical Bibliographies," by Paul Escher, 1920

Carnegie Library of Pittsburgh
Pittsburgh, Pa.
September 18, 1920

E. H. McClelland

EXPLOSION OF FLASHLIGHT POWDERS

Editor of the Journal of Industrial and Engineering Chemistry:

Recently a young student of my acquaintance, while experimenting with a "flashlight powder," which consisted of a mixture of potassium chlorate, sulfur, sodium carbonate, and red phosphorus, was so badly injured by an explosion that it was necessary to amputate his right hand.

In order to avoid repetition of such an explosion, or other explosions closely similar, students of elementary chemistry, particularly high-school students, ought to be emphatically warned against the danger existing in mixtures of oxidizing agents with either sulfur or red phosphorus, or with both. Furthermore, it is the duty of high-school chemistry teachers to discourage any attempt on the part of their pupils to experiment with flashlight powders, gunpowder, fireworks, semiexplosives, and the like.

Richard H. Kerbs

192 Wilkins Street
Rochester, N. Y.
August 21, 1920

COMPOSITION OF WATER-GLASS SOLUTIONS

Editor of the Journal of Industrial and Engineering Chemistry:

Whenever the results of scientific work involving sodium silicate solutions are published, care should be taken to record the composition of such solutions.

The appellation "water glass" covers materials which differ greatly in composition and properties. Mr. Vail's recent article[1] will give an excellent idea of these variations.

Attention was called to this matter by the article on "The Preservation of Eggs" by Jones and DuBois in the August 1920 number of This Journal. The omission was particularly unfortunate in this case because the silicate solution was used as a standard. The more alkaline a solution is, the less satisfactory it is as an egg preservative. The presence of small amounts of sulfur compounds often causes spoilage.[2]

The confusion that exists in regard to sodium silicate is shown in two articles by Schurecht. In the first,[3] he states that the sodium silicate used "corresponded to the formula $Na_2O.\ 3.1SiO_3$," yet the lines in his graphs of the results were marked "Na_2SiO_3." In a later article,[4] he gives graphs with the lines marked "Na_2SiO_3" but no explanation is given. On account of the first article the question arises, what was the composition of the sodium silicate used in the later work?

All through the literature similar confusion is found. The value of the work done would be greatly exhanced by the inclusion of data sufficient to enable one to duplicate conditions. The gravity and the percentages of Na_2O and of SiO_2 should be determined.

One reason for the lack of analytical information may be the long procedure for analysis usually given in textbooks. The alkali may be determined by titration with standard acid with methyl orange as an indicator. A quick, fairly accurate method for water was devised by Ordway, in which the sample is added to an amount of ignited calcium sulfate equal to twice the weight of the Na_2O present. The mixture then is dried to constant weight. The percentage of silica is equal approximately to $100 - $ (per cent Na_2O + per cent H_2O).

William Stericker

Mellon Institute of Industrial Research
Pittsburgh, Pennsylvania
August 27, 1920

AUTOMATIC METHODS OF GAS ANALYSIS DEPENDING UPON THERMAL CONDUCTIVITY

Editor of the Journal of Industrial and Engineering Chemistry:

My attention has been called to an article in the April 1920 issue of the Journal, by Messrs. Weaver, Palmer, Frantz, Ledig and Pickering, on automatic methods of gas analysis. May I be allowed to state one or two facts in reference to my katharometer which is referred to in the article?

In giving an historical account of thermal conductivity methods of gas analysis your contributors have referred to U. S. Patent 1,304,208 (1919) for details of my katharometer. They appear not to have known that the British patent was applied for in January 1916 and was granted after the instrument had been fully developed in its present form. The katharometer was devised in the Physics Department of the University of Birmingham in 1915 to meet a war emergency, under restrictions as to money, labor, and literature imposed by circumstances. I was, therefore, in ignorance of any previous work on the subject.

This greatly alters the history as given by your contributors. The successful commercial form of the katharometer is clearly earlier than the instruments of the Sperry Gyroscope Company, the Bureau of Standards, and the University of California, although it was unknown to those workers.

The instrument has been made and sold by the Cambridge Scientific Instrument Company for some years, and has given very satisfactory service in France and other theatres of the war, as well as in research work. Some results of this work have been communicated to the Advisory Committee for Aëronautics, from 1916 onwards.

In the summer of 1918 I presented to the Bureau of Standards a katharometer and balloon-fabric permeability tester.

The balanced bridge is no novelty; it was the first I tried and I still use it in research work. The patent specification purposely leaves this point open and covers the form described in the Journal.

The balanced bridge form was shown to the British Admiralty in 1915, but as a fixed bridge proved much more useful for practically all commercial purposes and was most easily adapted for indicating and automatic recording, and for central reading of instruments at various distant points, it has been most generally used.

All the future work spoken of by the Bureau is already in hand here and much of it has already been finished. The Bureau will find as it proceeds with its experiments that the form which it has adopted has several disadvantages which are not at first sight apparent. These points cannot be satisfactorily dealt with in a letter, but those interested may find some information on the subject in a recent paper on the theory of the katharometer by Dr. H. A. Daynes in the *Proceedings of the Royal Society.*

I believe that the katharometer was the first instrument in which the effect of thermal conductivity was used in a practicable and remarkably accurate form for purposes of gas analysis.

The University
Birmingham, England
July 17, 1920

G. A. Shakespear

. . . .

Editor of the Journal of Industrial and Engineering Chemistry:

I do not wish to dispute any of the statements regarding the history of the thermal conductivity method of gas analysis contained in the preceding note by Professor Shakespear. Several of the facts stated by Professor Shakespear were not known to me, however. Accepting in full Professor Shakespear's statement of the facts, the only change which seems necessary in the article referred to is the description of the instrument developed at the University of California as "earlier" than Professor Shakespear's instrument. Since the former was known to us about a year before we heard of Shakespear's work, and since Shakespear's British patent was kept secret for military reasons, this mistake was only natural.

The first experimental work along this line was done at the Bureau of Standards in the late summer and autumn of 1915, following the work of Koepsel who was the real pioneer with this method; but as previously stated nothing practical was accomplished. The work had been resumed with every prospect of success and nearly the present form of apparatus had been evolved when we first heard of Professor Shakespear's work, through military channels, about the first of March 1918. The first intelligible description of the apparatus was not received until a month or more later. At that time we wrote to Professor Shakespear describing our own work and referring to the earlier investigators whose work was known to us. No reply was received to this or to at least one later letter. All correspondence was, however, through devious official channels, and our failure to get in direct communication with Professor Shakespear may have been due to no fault of his own.

The instruments developed by Professor Shakespear which are known to us, *viz.*, the "katharometer" and the "permeameter," are beautifully constructed instruments well adapted to the purposes for which they are intended.

The "katharometer" is designed to sample and determine the amount of air in balloon gas, and is certainly one of the best instruments ever devised for the purpose. The "permeameter" is designed to test the permeability of balloon fabrics and works well, although we do not regard it as a satisfactory substitute for the methods employed at this Bureau. A great deal of credit is due to Professor Shakespear for his work in developing these instruments, the more so because he had no knowledge of the similar work of Koepsel and of Siemens and Halske, of which we took advantage.

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[1] This Journal, 11 (1919), 1029.

[2] *Chem.-Ztg.*, 42, 195.

[3] *Trans. Am. Cer. Soc.*, 19 (1917), 460

[4] *J. Am. Cer. Soc.*, 1 (1918), 201.

There may be room for difference of opinion upon the relative merits of the balanced and unbalanced bridge in connection with this method. We stated our reasons for preferring the former, at least for certain classes of work, and there is nothing in Professor Shakespear's statement to modify our opinion.

The truly remarkable thing in connection with the history of this method is that a method capable of such great accuracy and such a wide variety of important applications should remain practically unknown to the technical world for at least ten years after its simplicity, accuracy, and some of its important applications were pointed out by Koepsel. This is especially strange in view of the fact that an instrument having useful properties is not at all hard to make, as shown by the five or six independent investigators who have obtained good results with apparatus of very different form.

Bureau of Standards
Washington, D. C.
August 26, 1920

E. R. Weaver

STOLEN PLATINUM

There were recently stolen from the laboratory of the North Dakota Agricultural College, Agricultural College, N. D., four platinum evaporating dishes and four platinum crucibles. The weights and markings on the evaporating dishes were as follows:

Marking	Weight Grams
Z-1	31.0580
S-2	32.6527
RH-1	20.8457
S-3	20.9213

The four platinum crucibles taken from the laboratory were marked and weighed as follows:

Marking	Weight Grams
I	19.3082
II	14.9760
III	15.8049
IV	14.8500

The total weight of the platinum stolen at this time was 170.4168 g. Two platinum dishes had previously been stolen from the laboratory at the Agricultural College.

NEW CHEMICAL LABORATORY FOR YALE UNIVERSITY

Plans are now being prepared for a new building for the Department of Chemistry of Yale University, which has hitherto carried on its work partly in the Kent Chemical Laboratory and partly in the Sheffield Chemical Laboratory. According to present plans, the new building will be located on the Pierson-Sage Square, just north of the Sloane Physics Laboratory, where ample space is available. It will have a total floor area of 100,000 square feet; and, in addition to the usual laboratories and recitation rooms, will include an ample number of rooms for research work, as well as space in which it will be possible to develop a process from the laboratory investigation up to a small-sized commercial scale.

NEW EXPERIMENT STATION OF THE BUREAU OF MINES

The Bureau of Mines is to open a new mining experiment station, with headquarters in St. Louis, Mo. The actual laboratory and investigational work will be done in coöperation with the Missouri School of Mines and Metallurgy at Rolla, Mo.

The new station will devote special attention to the problems of lead and zinc production in the Mississippi valley, and particularly to the development of a metallurgical process for the recovery of lead from the oxidized ores, which exist in large deposits in certain districts of Missouri.

GASOLINE FROM NATURAL GAS. III—HEATING VALUE, SPECIFIC GRAVITY, AND SPECIFIC HEAT—CORRECTION

In the article of the above title [This Journal, 12 (1920), 852] Equation 3 should read as follows:

$$\text{B. t. u. per lb.} = 1.8\left(\frac{158{,}650n + 53{,}200}{14.016n + 2.016}\right)$$

Oil City, Pa.

R. P. Anderson

ALKALI FUSIONS. II—THE FUSION OF SODIUM BENZENE *m*-DISULFONATE WITH SODIUM HYDROXIDE FOR THE PRODUCTION OF RESORCINOL—CORRECTION

In the article of the above title [This Journal, 12 (1920), 857] the following correction should be made:

Page 859, first column, first sentence should read: "The total amount of sulfate sulfur in Solution B found by this determination was deducted from the total sulfur found by sodium peroxide fusion method, and the result calculated as $C_6H_4(SO_3Na)_2$."

Washington, D. C.

Max Phillips and H. D. Gibbs

THE PREVENTION OF SUGAR DETERIORATION BY THE USE OF SUPERHEATED STEAM IN CENTRIFUGALS—CORRECTION

Through an error in printing, Fig. 1 of Dr. Kopeloff's article [This Journal, 12(1920), 860] was inverted.

WASHINGTON LETTER

By J. B. McDonnell, Union Trust Building, Washington, D. C.

TARIFF COMMISSION DYESTUFFS REPORT

The year 1919 witnessed considerable progress on the part of the American dye industry as compared with the previous year, as disclosed by the census of dyes and other coal-tar chemicals which is nearly ready for publication by the United States Tariff Commission. Total production during 1919 was 63,000,000 pounds, valued at $67,000,000. During 1918 production amounted to 57,000,000 pounds, valued at $61,000,000.

Publication of the report has been delayed this year beyond the date it was completed last year, when it appeared in June. While some few reports still have not reached the Tariff Commission, these are mostly from small concerns. These additional schedules may make some slight changes in the figures as shown at present, but it is safe to say that no very material change will be made in the present figures, which show clearly certain very interesting features.

Dr. Grinnell Jones, who has been in Washington recently in connection with completion of the census, will make public many of the details of the census in an address which he will deliver at the National Exposition of Chemical Industries in New York during the coming week.

CHEMICAL WARFARE SERVICE ADVISORY COMMITTEE

But little has been heard as yet of the appointment of a committee composed of some of the most eminent chemists in the country to act in an advisory capacity to the chief of the Chemical Warfare Service, General Amos A. Fries. The committee was appointed at the Chicago meeting of the American Chemical Society, and is headed by Dr. Chas. H. Herty, as chairman. Dr. Herty has conferred with General Fries regarding the work of the committee. There will be no public discussion of the work of the committee; it will be a great, all-powerful, if silent and but little heard-of, body working for the national defense.

Plans for inauguration of work of startling sweep now are in the making and may be announced within the next few weeks. While these do not have to do with the Chemical Warfare Service Advisory Committee, they are of intense interest not only to the chemists, but to every doctor of medicine in the country, and the general public. It is contemplated to utilize the Chemical Foundation to father this work, which will revolutionize the whole science of medicine giving.

SALE OF SURPLUS STOCKS OF GERMAN DYES

It is understood that efforts are now being made to establish workable machinery through which consumers who have found themselves with larger quantities of German dyestuffs than they actually need may dispose of their surplus and purchase from each other without disclosing to competitors just what they are doing. Investigation was recently inaugurated by the Department of Justice at the request of the War Trade Board Section of the Department of State into the offering for sale of German vat dyes by concerns which had made no application for selling permits to the War Trade Board. It was discovered that several consumers had on hand larger quantities of certain dyes than they expected to use and wished to dispose of some of them. Many of them apparently did not know that the regulations of the Board demanded issuance of a permit to sell such dyes. The matter has not yet been definitely settled, according to officials here, but establishment of a central office which shall act as a clearing house for such dyes has been suggested and discussed. Under the proposed arrangement names of consumers offering dyes for sale and those purchasing them would be kept secret.

THE INDUSTRIAL ALCOHOL SITUATION

Apparently there has been no change in the industrial alcohol situation here. The matter is officially in the status it has occupied since the conference held here some time ago with internal revenue officials. It was reported that Commissioner Williams has decided to ask Congress when it meets in December to entirely divorce industrial alcohol from the prohibition enforcement law, and to provide adequate machinery for handling the industrial alcohol question alone.

Among those interested in seeking relief for the hampered industry, however, it is contended that Commissioner of Internal Revenue Williams has ample authority under existing law to take steps which would relieve the industry from its burden. It is specifically provided in the present law, it is pointed out, that development of the industrial alcohol industry is to be fostered.

The United States has decided that it will not exercise its option on impounded German drugs and chemicals, it was announced recently by the War Trade Board, although the right to exercise its option on the daily production after July 1 still is maintained. The decision of the Board was announced just prior to the expiration of the time limit set for definite action, and was taken because of the lack of demand for these German goods in this country.

While the United States has no legal right to participate in the distribution of German dyes and chemicals under the treaty of peace, its moral right is such that it will be considered as having full rights in this direction, it has been decided by the interallied commission in Paris, according to reports reaching here.

Publication of the dyes and chemicals imported into this country, as shown by licenses granted by the War Trade Board, is a probability of the near future. Some discussion took place regarding the inclusion of this information in the dye census of the Tariff Commission, but the present decision is that this information shall be published by the War Trade Board. Such publication would afford very valuable statistics for purposes of comparison with pre-war import figures.

September 18, 1920

PARIS LETTER

By Charles Lormand, 4 Avenue de l'Observatoire, Paris, France

The universities and research laboratories are just now closed for vacation, and news of pure science is scarce. However, I can announce in the realm of pure chemistry the work of M. Lacroix, perpetual secretary of the Académie des Sciences, who has found considerable amounts of scandium in Madagascan minerals of the same family as cymophane. Up to this time, this element has remained in the domain of spectroscopy. The high content in these minerals will permit a complete study by the simplest chemical means. It seems that it might be well for American geologists and chemists to search for scandium in the rocky regions of the West and the Far West (Colorado or Utah).

THE COAL AND IRON PROBLEM

The coal mines in northern France are not yet reconstructed, and the difficulties in the delivery of German coal are turning the manufacturer toward processes involving fuel economy.

The ferrous metallurgical industry is extremely interested in a new process which has caused much discussion. The process has not been reported before the Académie des Sciences or before any of the chemical societies. It consists solely of a series of patents, ten in number, taken out by the inventor of the process, M. Basset. These patents apply to the direct manufacture of iron and steel without the use of the blast furnace, or the Martin, Thomas, or electric furnaces. It is a direct transformation, in a single apparatus, from the mineral to the steel or iron.

A company with a capital of 60,000,000 francs (Société Française des Aciéries de Basset) has been formed, and the first tests have been made at Mantes, in an old cement factory, working with the rotating furnace there installed. The patents call for the rotating furnace of the present model. In these tests a daily production of 25 tons has been obtained.

It is planned to install 6 furnaces of 250 tons capacity at Longwy, near the Lorraine valley, given to France by the treaty of Versailles. A factory capable of producing 2,000 tons per day is also planned in Normandy near Caen, where during the last decade numerous new bearings of iron minerals have been discovered.

It would seem that the tests at Mantes have been entirely satisfactory and the general application of the process should bring about a considerable revolution in the siderurgical industry. A comparison of the heat balance of the old and the Basset processes shows that to produce a ton of cast iron 1400 to 1500 kilos of coal are needed for the old method and 900 kilos for the Basset. This saving seems slight, but the Basset process permits the use of any fuel. Moreover, the rotating furnace permits the use of powdered minerals, since the velocity of the air in the furnace is very slow and the great air pressure in the blower, necessary in the blast furnace, is replaced in the rotating furnace by an air injector of very low power.

The weakness of the process seems to lie in the necessity of using mineral of high iron content. The tests at Mantes were made with roasted pyrite. Nothing is known of how the minerals of Lorraine and Normandy will behave.

The originality of the process consists in the better utilization of the carbon monoxide or rather of the coal, since the coal is introduced into the center of the furnace in the form of dust by means of a current of air.

Opinions upon the value of the different patents covering the process are varied, but, neglecting this point, our attention will be fixed on the results at the Lorraine factory.

Along the same line I may mention the work done in the region of the Alps, where electric energy is obtained from the waterfalls, and where electrolytic iron is being produced by using the mineral in an appropriate solution. This is another very interesting attempt to escape from the coal problem. The factories producing electrolytic iron are situated in the region of Grenoble, and one of them has just ceded its process to Italian metallurgists on the other side of the Alps.

THE NITROGEN PROBLEM

The conference by M. Georges Claude, of which I spoke in my first letter, was a very great success. M. Claude showed the possibility of obtaining ammonia by the use of what he calls "hyperpressures," which reach 1,000 atmospheres. The obtaining of these hyperpressures does not seem to involve a very high net cost. The heat produced makes the reaction more smooth, and simplifies the extraction of the ammonia.

Granting these theoretical advantages, there is to be noted in the process the difficulty of obtaining tight joints, a difficulty which M. Claude has perfectly solved by the use of cup-leather joints. These joints, resistant to hyperpressures, will open to investigators a new field, for the use of hyperpressures is still in its infancy.

Since the starting material, nitrogen, is easily obtained by the liquefaction of air, the question of the other ingredient, hydrogen, must be considered. M. Claude mentions as a solution of the problem gas from coke ovens, illuminating gas, or water gas. Extraction of hydrogen from this gas seems to be practicable. However, we would note one point upon which M. Claude has not been very exact; that is, the economical extraction of the hydrogen. It is necessary to use very pure hydrogen in order not to diminish the efficiency of the catalyzer, which rapidly becomes exhausted; and such purification of hydrogen from these sources has not yet been completely realized.

September 9, 1920

INDUSTRIAL NOTES

According to a recent announcement the Bureau of Standards is in need of the services of several well-qualified young chemists for work in various lines. Candidates who have had graduate work or special experience in physical chemistry are especially desired. No examination is required. The entrance salaries will range from $1400 to $2400 per annum, depending upon the qualifications of the applicant. Applicants should write to the Civil Service Commission for Announcement 2236 and Form 1312, and should also communicate directly with the Bureau of Standards.

At the recent meeting of the American Dyes Institute the following committee on the nomenclature, spelling, and pronunciation of chemical products as applied to the dyestuffs industry was appointed: Mr. J. Warren Kinsman of E. I. du Pont de Nemours & Co., Dr. D. W. Jayne of The Barrett Co., Mr. J. R. M. Klotz of the Newport Chemical Works, Inc., Dr. J. M. Matthews of the Grasselli Chemical Co., and Mr. L. H. Cone of the National Aniline & Chemical Co. The Committee on Sanitation and Safety, composed of Mr. Victor L. King and Mr. Moses Crossley of the Calco Chemical Co., Mr. George B. Bradshaw of E. I. du Pont de Nemours & Co., and Albert G. Peterkin of The Barrett Co., made a report of its Philadelphia meeting, which included preliminary study of a plan outlined by Dr. Francis D. Patterson, chief of the Division of Industrial Hygiene and Engineering of the Department of Labor and Industry of the State of Pennsylvania.

The Bureau of Mines has completed arrangements for a coöperative research on the carbonization of lignite. $200,000 is to be supplied by private parties for the erection of a plant at New Salem, N. D. The Bureau of Mines will be in charge of the technical and experimental side of the investigation.

Because of the scarcity of limestone for use in the manufacture of sulfurous acid, on account of car shortage and other reasons, six of the largest paper companies in New York have organized the Richville Limestone Company to operate the limestone quarries at Richville, N. Y. A 38-year lease of the quarries has been taken, and the necessary machinery and equipment will be installed immediately. The corporations forming the combination are the Dexter Sulphite Pulp and Paper Co., of Watertown, the Newton Falls Paper Co., of Watertown, the Carthage Sulphite Pulp & Paper Co., of Carthage, the Oswego Falls Pulp & Paper Co., of Fulton, the De Grasse Paper Co., and the Gould Paper Co., of Lyons Falls.

The Newport Chemical Company is shortly to begin the erection of two large factory buildings in Passaic, N. J., which will cost in excess of $200,000. The present buildings will be abandoned when the new ones are completed.

The Honorary Advisory Council for Scientific and Industrial Research of Canada has awarded $5,000 to assist Prof. J. C. McLennan of Toronto University in investigations on helium, to determine its uses for lamps, amplifying values, high resistances, etc. One of the chief objects is to discover a method of conservation to prevent the present wastage which is estimated at 1,000,000 cu. ft. per month.

The Italy-America Society has announced that an American has secured from the Italian government a concession for the utilization of 800 h. p. of the waterfalls at Terni, 70 miles from Rome, for the production of nitrogenous plant food. Synthetic ammonia manufactured by water power at Terni has already been put on the market on a paying basis. With its present equipment the plant is capable of producing one ton of ammonia daily.

A new course in textile engineering is to be added at North Carolina College. This will make the fourth course offered by the textile department, as follows: Four-year course in textile manufacturing, four-year course in textile engineering, four-year course in textile chemistry and dyeing, and two-year course in textile manufacturing.

The Mathieson Alkali Works, Inc., has established a western district sales office at 327 South LaSalle St., Chicago, Ill.

The 1919 report of the English National Physical Laboratory, which has just been issued, contains the report of the executive committee for 1919, the statement of work proposed for 1920–21, a list of papers published by the laboratory during 1917, 1918, and 1919 or communicated by members of the staff to scientific societies or technical journals, and the report of the director for 1919.

The Netherlands Dyestuffs Factory has recently been established at Amsterdam with the coöperation of large industrial and banking concerns, to promote the manufacture of dyes and intermediates which were formerly chiefly imported from Germany. Attention has been particularly directed to the preparation of ethereal oils, essences and perfumes, inorganic and organic acids and salts, medicines, tar distillates and their derivatives, including aniline dyes.

The production of bituminous coal in the United States for the 199 working days ending August 21, 1920, as compared with corresponding periods in previous years was as follows:

	Tons
1917	352.011,000
1918	375.395.000
1919	287,270.000
1920	335,967,000

The production of anthracite up to August 21, 1920, was 55,712,000 tons, as compared with 52,678,000 in 1919. The coal production for the first three months in Canada was 4,126,523 tons in 1920, as compared with 3,735,654 in 1919.

The Commission appointed by Supreme Court Justice J. F. Minturn to investigate the damages to dyeing companies resulting from the diversion of water from the Passaic River has awarded $302,852 to the Wiedmann Silk Dyeing Company and the National Silk Dyeing Company. $97,351 are levied against Jersey City, $48,675 against Newark, and $5,400 against the Acquackanonck Water Company. Counsel for the municipalities has given notice that the case will be appealed from the award of the commissioners.

The report of the Commissioner of Patents shows that during the fiscal year ending June 30, 1920, 81,948 applications for inventions were filed, as compared with 62,755 during the previous year. The total number of applications of all kinds was 102,940, which is 27,283 more than in 1919. The cash receipts from all sources amounted to $2,615,697.33, and the total expenditures to $2,436,561.37, leaving a net surplus of $179,135.96.

The seven months' exports from London to the United States, January to July 1920, showed: Drugs and chemicals, $6,462,593 as against $3,574,541 in 1919; gums, $3,002,037, as against $997,604 in 1919.

At the August meeting of the American Institute of Fertilizer Chemists, which was organized at the annual meeting of the National Fertilizer Association in June, the details of the organization were discussed and the aims and purposes of the Institute were formulated.

The Canadian government has made experiments which prove the practicability of making paper from flax straw. The flax crop of Canada in 1919 would have produced 1,000,000 tons of straw which would have made 100,000 tons of pulp for paper, thus relieving the drain on the forests. Manufacturers have signified their intention of coöperating with the government.

During the last seven months of 1919 dyes were manufactured in France as follows:

	TONS
June	175
July	231
August	270
September	326
October	441
November	410
December	602

These were divided as follows: Acid colors, 121 tons; basic colors, 10 tons; direct colors, 48 tons; sulfur colors, 175 tons; indigo, 225 tons.

Exports of aniline dyes from the United States for the six months ending in June 1920 totaled $10,855,959, the totals per month being as follows:

	Dollars
January	917,574
February	1,850,662
March	2,648,401
April	1,829,771
May	2,120,606
June	2,389,515

The following table shows the distribution of dyes by countries for the months of May and June:

	MAY	JUNE
Japan	$625.607	$680,215
China	109.503	622,345
Mexico	124.828	4.229
British India	133,155	199,036
Canada	193,211	188,731
France	112,375	134.705
Italy	72,020	40.803
Spain	155,293	110.340
England	136,659	128,353
Argentina	124,571	38.893
Brazil	51,492	43,840

One man was killed and several others injured by a fire which destroyed the percolating building of the Toledo Seed & Oil Company recently. The damage is estimated at $50,000.

The first factory for the manufacture of sulfuric acid in Uruguay has been established by the Instituto de Quimica Industrial at Capurro, and has already commenced production at the rate of 3,500 kilograms daily. Nitric, hydrochloric, and other acids are to be manufactured later.

The Stellar Company of Minnesota, organized to extract turpentine from pine stumps, is ready for operation. The plant is to run night and day and shipment of turpentine, creosote, pine oil, rosin oil, boiled tar, and charcoal is to begin at once. Three or four carloads of Norway pine will be used each week.

The creation of an All-India Chemical Service with a central research institute at Dehra Dun and laboratories in each province has been recommended by a committee presided over by Professor J. F. Thorpe of the Imperial College of Science and Technology, London. The object is to assist by scientific investigation in overcoming the difficulties and deficiencies in Indian industrial organization. It is intended that the research staffs shall be composed mainly of Indians, so far as those with adequate training are available.

A gas obtained from the destructive distillation of straw is being produced on a small scale at the experimental farm of the U. S. Department of Agriculture at Arlington, Va. The gas has been used for motor fuel, and for illuminating and cooking purposes, but its commercial value has not been determined. Fifty pounds of straw will produce about 300 cu. ft. of gas, and the Office of Development Work is working on the problem of liquefying or condensing the gas to enable it to be used practically as a motor fuel. Several valuable by-products are obtained in the process of manufacture.

About 106,000 tons of fuller's earth valued at $2,000,000 were produced in the United States in 1919. These figures show an increase of 217 per cent in quantity and of 563 per cent in value in 10 years, being an increase of 25 per cent in quantity and 74 per cent in value over 1918. Florida produced nearly nine-tenths of the 1919 output.

The mica mine at Blue Mountain, Stony Lake, Canada, has been purchased by American engineers who expect to start operations immediately, shipping 100 lbs. of mica a day.

Except for 6,000 tons of government guano per annum and a small supply of bone manure, the Union of South Africa is entirely dependent on foreign sources for artificial fertilizers. The total imports of manures and fertilizers in 1919 amounted to 12,617 tons.

PERSONAL NOTES

Mr. George A. Brewster, an active member of the AMERICAN CHEMICAL SOCIETY, the American Steel Treaters Society and the American Institute of Mining and Metallurgical Engineers, died August 17, 1920. Mr. Brewster was born in 1877, was educated at Ohio Northern University and held various positions in connection with the chemical industry, his last connection being with the American Radiator Co., of Buffalo, N. Y., as chief chemist.

Mr. John A. Dawson, one of the charter members of the California Section of the AMERICAN CHEMICAL SOCIETY and one of the oldest chemists on the Coast, died recently. Mr. Dawson was educated as a pharmaceutical chemist, and early in life became connected with the U. S. Customs House in San Francisco as examining chemist for foreign imports, serving in this capacity for thirty years.

Dr. Harmon N. Morse, professor of chemistry and director of the chemical laboratory at Johns Hopkins University, died recently at his summer home on Chebeague Island, Me. Dr. Morse was born in Cambridge, Vt., in 1848. After his graduation from Amherst College in 1873 he studied at the University of Göttingen and returned to Amherst as an assistant in chemistry in 1875. He went to Johns Hopkins as an associate professor in 1876.

Mr. Russell W. Moore, past president of the Chemists' Club, died on July 31 at his home, 44 West 77th St., New York City.

Mr. George P. Gray has resigned his position as assistant professor of entomology and chemist, insecticide laboratory, at the University of California, to become chief of the Division of Chemistry of the newly established Department of Agriculture of the State of California, Sacramento, Cal.

Mr. Daniel H. Simpson has resigned his position in the physical chemistry section of the Bureau of Standards, Washington, D. C., and is now in the sales division of the Edison Electric Appliance Co., Inc., Chicago, Ill.

Mr. A. J. Gailey has left the W. L. Cummings Chemical Co., Lansdowne, Pa., to accept the position of research chemical engineer for the Electrometallurgical Co., Niagara Falls, N. Y.

Mr. Florian A. Cajori, formerly Captain in the food section of the Sanitary Corps and on duty in Jugo-Slavia with the American Relief Administration, has completed his graduate work at Yale University and accepted a position as instructor in physiological chemistry at Leland Stanford, Jr., University, in California.

Mr. Thorwald A. Carlson has completed his work in connection with his Metallurgical Research Fellowship in the Department of Metallurgical Research, University of Utah, and is now in the testing department of the Anaconda Copper Mining Co., Anaconda, Mont.

Mr. G. E. Daibey has resigned his position as superintendent of the smelting plant of Benj. Harris & Co., Chicago, Ill., and is now with the Eastern Brass & Ingot Corporation of New York, Waterbury, Conn.

Mr. C. E. Vail has resigned his position as chemist with the Empire Refineries, Inc., Okmulgee, Okla., and is now assistant chemist on the staff of the Colorado Experiment Station, Fort Collins, Col.

Mr. R. T. Haslam has left the National Carbon Company, Cleveland, Ohio, to become director of the School of Chemical Engineering Practice of the Massachusetts Institute of Technology, Cambridge, Mass.

Dr. Harrison E. Patten, for several years research chemist with the Bureau of Chemistry of the Department of Agriculture, Washington, D. C., has accepted the position of chief chemist of the phosphate plant of the Provident Chemical Works, St. Louis, Mo.

Mr. Lewis C. Slater has resigned as assistant professor of industrial and engineeridg chemistry at Louisiana State University, and is now chemist for the Bogalusa Paper Co., Inc., Bogalusa, La.

Mr. DeWitt O. Jones, formerly in charge of the research laboratory of Armour Fertilizer Works, U. S. Yards, Chicago, Ill., has taken a position with the Newport Company, Carrollville, Wis.

Mr. Charles H. Breed, until recently metallurgist with the Crown Cork & Seal Co., Baltimore, Md., has joined the staff of Daniel M. Luehrs, industrial consulting engineers, Cleveland, Ohio, as consulting metallurgist in charge of the metallurgical laboratories.

Mr. F. L. Righter, for the past year a graduate student in the chemistry department of Cornell University, has joined the staff of the research laboratory of the Eastman Kodak Co., Rochester, N. Y.

Mr. David Jones, holder of an 1851 Exhibition Scholarship from London University at Johns Hopkins University, is at present with the chemical division of the Eastman Kodak Co., Rochester, N. Y.

Mr. Lester A. Buehler has accepted a position as assistant in the Department of Operative Pharmacy in the Philadelphia College of Pharmacy and Science, Philadelphia, Pa.

Mr. Kenneth A. Brownell, formerly assistant chemist for the Sayles Finishing Plants at Saylesville, R. I., has accepted a position as chemist for the Standard Bleaching Co., of Carlton Hill, N. J.

Mr. J. D. Brown has left the Johnson City High School, Johnson City, Tenn., to become supervisor of the aniline department of the Union Dye & Chemical Corporation, Kingsport, Tenn.

Mr. E. M. Heumann, until recently connected with the Crown Cork & Seal Co., Baltimore, Md., is in charge of the chemical laboratories of Daniel M. Luehrs, industrial consulting engineers, Cleveland, Ohio.

Mr. J. B. Ferguson has left the research laboratories of the Western Electric Co. of New York City to accept an appointment as associate professor of research chemistry at the University of Toronto, Toronto, Canada.

Mr. Arthur Bridge, for eight years chemist for the Central of Georgia Railway, Savannah, Ga., has accepted a position with the Newport Chemical Co., Carrollville, Wis., where he is engaged in the manufacture of coal-tar dyes.

Mr. Floyd K. Thayer has accepted a position as organic research chemist for the Abbot Laboratories, Chicago, Ill.

Mr. Lester Yoder, formerly assistant chemist in the Iowa State Experiment Station, is now assistant in the research division of Parke, Davis & Co., Detroit, Mich.

Mr. J. R. Ruby, for three years in charge of the rubber research work of the New Jersey Zinc Co., has associated himself with Mr. C. P. Hall at Akron, Ohio, dealing in pigments and chemicals for the rubber trade.

Mr. Wallace F. Super, who received the degree of B.S. in chemical engineering from the University of Pennsylvania in June 1920, is connected with the Atmospheric Nitrogen Corporation at Laurel Hill, Long Island, N. Y.

Mr. L. E. Elliott, formerly water engineer, Wabash R. R., Decatur, Ill., is at present employed in a similar capacity with the St. Louis-San Francisco R. R., Springfield, Mo.

Mr. B. I. Corson, chemical engineer, has severed his connection as chief chemist with the Durkee Atwood Co., Minneapolis, Minn., and has accepted a position in the research laboratory of Hemingway & Co., Bound Brook, N. J.

Mr. Morris A. Pozen has resigned as chief chemist, Health Department, Washington, D. C., to accept a similar position with the Schwarz Laboratories, analytical and consulting chemists, New York City.

Mr. Ewing C. Scott, having fully recovered from a siege of illness after his discharge from the Army, has accepted a position in the laboratory of the Phelps Dodge Corp., Morenci, Ariz.

Mr. Zoltan de Horvath resigned from the employ of E. I. du Pont de Nemours & Co., to become chief chemist of the Midland Chemical Co. of Argo, Ill.

Mr. Jason L. Russell, formerly chemist with the Swan-Myers Co., Indianapolis, Ind., is now connected with Frederick Stearns & Co., Detroit, Mich., where he has charge of the analytical work.

Mr. L. E. Jackson resigned as chemist and chemical engineer with the Empire Gas & Fuel Co., Bartlesville, Okla., and has accepted a fellowship with the Mellon Institute, Pittsburgh, Pa.

Mr. W. W. Peters, formerly chemist for Dow & Smith, consulting chemical engineers of New York City, has joined the forces of the Beacon Oil Co., Boston, Mass., as assistant chief chemist.

Mr. Lewis W. Armstrong has left the Wisconsin Chemical Products Co., Shawano, Wis., where he was chief chemist, and has become superintendent of laboratories of Kimberly-Clark Co., Niagara, Wis.

Dr. Walter T. Taggart, for many years professor of organic chemistry at the University of Pennsylvania, has been elected to succeed **Dr. Edgar Fahs Smith** as Blanchard Professor of Chemistry at that institution. Dr. Smith resigned as Provost and Professor of Chemistry last June. Professor Taggart is now the head of the chemical department of the University.

Dr. Nicholas Kopeloff has left the Sugar Experiment Station, Louisiana State University, and has accepted the position of associate in bacteriology at the Psychiatric Institute of the New York State Hospitals. He will conduct research on the possible correlation between bacterial infections and mental derangements.

Mr. D. C. Leander Sherk, Ph.D. University of Wisconsin, June 1920, is employed as research chemist with the Gillican-Chipley Co., Inc., New Orleans, La.

Mr. Herbert S. Bailey has resigned his position with E. I. du Pont de Nemours & Co., where he has been in charge of research paints, varnishes, lubricating, and heating oils, to accept a position as assistant chief chemist in charge of research work of the Southern Cotton Oil Co., Savannah, Ga. Mr. Bailey is editor of the Chemists' Section of the Cotton Oil Press.

Mr. Walter R. Kirner, M.S. University of Illinois, is now associated with the synthetic chemistry department of the Eastman Kodak Co.'s research laboratory, Rochester, N. Y.

GOVERNMENT PUBLICATIONS

By Nellie A. Parkinson, Bureau of Chemistry, Washington, D. C.

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

FEDERAL BOARD FOR VOCATIONAL EDUCATION

Coal Mine Ventilation. R. Z. Virgin. Bulletin 41. Trade and Industrial Series 11. 64 pp. Paper, 10 cents. 1920.

NATIONAL ACADEMY OF SCIENCES

Fourth Annual Report of National Research Council. 68 pp. 1920.

WAR DEPARTMENT

Airship and Balloon Gas Manual. Book 1. War Department Document 985. 160 pp. Paper, 25 cents. 1920.

Airship and Balloon Gas Manual. Book 2, Gas Plant Operation. War Department Document 985. 51 pp. Paper, 5 cents. 1920.

Comparative Test of Special Homogeneous Gasoline and Commercial Aëronautic Gasoline. Power Plants Report 85. 4 pp. 1920. Air Service Information Circular, Heavier-than-Air, Vol. I, No. 35.

PUBLIC HEALTH SERVICE

Prompt Shipment of Water Supply Chemicals Assured. 35, 2059. The Commission on Car Service of the American Railway Association, which is associated with the Interstate Commerce Commission, has instructed railroads to move promptly the following materials when they are to be used for the purification of public water supply, or when for movement to plants for the manufacture of chemicals to be used for such purposes: Aluminium, sulfate, bauxite, chlorine, calcium hypochlorite, soda ash, copperas, lime, and empty cylinders for chlorine shipment.

Botulism from Eating Canned Ripe Olives. Chas. Armstrong, R. V. Story and Ernest Scott. Reprint No. 577 from the Public Health Reports. 31 pp. Paper, 5 cents. 1920.

Note on the Hygienic Laboratory Method of Standardizing Disinfectants. Reprint No. 567 from the Public Health Reports. 3 pp. Paper, 5 cents. 1920.

GENERAL LAND OFFICE

Regulations Concerning Phosphate Leases and Use of Permits under the Act of February 25, 1920. Public No. 146, approved May 22, 1920. Circular 696. 20 pp. 1920.

Regulations Concerning Sodium Mining Leases and Prospecting Permits under the Act of February 25, 1920. Public No. 146, approved May 28, 1920. Circular 699. 24 pp. 1920.

GEOLOGICAL SURVEY

Gold and Silver in 1918. General Report. J. P. Dunlop. Separate from Mineral Resources of the United States, 1918, Part I. 55 pp. Published July 15, 1920.

Clay-Working Industries, Silica Brick and Building Operations in the Larger Cities in 1918. Jefferson Middleton. Separate from Mineral Resources of the United States, 1918, Part II. 88 pp. Published July 14, 1920. This report deals with the products of the clay-working industries, as well as with clay mining, and the tables are made up to show the output in their first form of manufactured clay products as best expressing the production of clay.

Platinum and Allied Metals in 1919. J. M. Hill. Separate from Mineral Resources of the United States, 1919, Part I. 10 pp. Published July 30, 1920.

Reports received from refiners of platinum, gold bullion, nickel, and copper indicate that 45,109 troy ounces of refined new metals of the platinum group were recovered in 1919, a decrease of 14,644 ounces, or 25 per cent, from the new metals recovered in 1918. About 11,759 troy ounces of the new metals recovered in 1919 are believed to have been derived from domestic materials.

New Platinum and Allied Metals Recovered by Refiners, 1915–1919, in Troy Ounces

Year	Platinum	Iridium	Iridosmine-osmiridium	Palladium	Rhodium
1915......	6,495	274	355	1,541	...
1916......	24,518	370	315	2,885	...
1917......	33,009	210	833	4,779	...
1918......	54,399	465	539	4,024	326
1919......	40,220	401	402	3,807	279

Magnesium in 1919. R. W. Stone. Separate from Mineral Resources of the United States, 1919, Part I. 4 pp. Published August 11, 1920. There were 127,465 lbs. of metallic magnesium manufactured in the United States in 1919, a decrease of 55 per cent in quantity and 60 per cent in value from the output of 1918. The production in 1919, however, was greater than in any year before 1918 and shows that the peace-time demands are increasing.

Bauxite and Aluminium in 1919. J. M. Hill. Separate from Mineral Resources of the United States, 1919, Part I. 8 pp. Published August 30, 1920. The quantity of bauxite marketed in the United States in 1919 was 376,566 long tons, a decrease from the production of 1918 of about 38 per cent in quantity and about 36 per cent in value. The domestic consumption was about 38 per cent less than that in 1918.

The value of primary aluminium produced in the United States in 1919 was $38,558,000, a decrease of about 6 per cent from the value of the output in 1918. The decrease was due largely to curtailment in production forced by the accumulation of large stocks in the preceding year.

Thorium, Zirconium and Rare-Earth Minerals in 1919. W. T. Schaller. Separate from Mineral Resources of the United States, 1919, Part II. 32 pp. Published September 1, 1920. The report aims to set forth the world relations, as well as the domestic resources of these minerals.

Fuel-Briquetting in 1919. F. G. Tyron. Separate from Mineral Resources of the United States, 1919, Part II. 4 pp. Published August 13, 1920. The total production of briquets in 1919 was 295,734 net tons, a decrease, compared with 1918, of 181,501 tons, or 38 per cent. In fact, the output dropped back to the position occupied in 1916.

Lithium Minerals in 1919. Herbert Insley. Separate from Mineral Resources of the United States, 1919, Part II. 4 pp. Published August 12, 1920. The output of lithium minerals in 1919 was ten times more than that in 1916. This marked increase is no doubt due to the increased use of lithium salts in storage batteries, and of lithium salts and lepidolite in the manufacture of glass.

The Mule Creek Oil Field, Wyoming. E. T. Hancock. Bulletin 716-C. Contributions to Economic Geology, 1920, Part II. 19 pp. Published July 27, 1920.

BUREAU OF MINES

Casing Troubles and Fishing Methods in Oil Wells. Thomas Curtin. Bulletin 182. Petroleum Technology 57. 48 pp. Paper, 15 cents. 1920. After expensive development work, many wells being drilled for oil have been abandoned, although the difficulties are sometimes susceptible of solution. This report attempts to classify these troubles and suggests solutions that will save the operator discouragement and expense.

Determination of Molybdenum. J. F. Bonardi and E. P. Barrett. Technical Paper 230. 35 pp. Paper, 5 cents. 1920. This report is the result of work done under coöperative agreements with the College of Mines, University of Washington, and the Colorado School of Mines. It points out certain disadvantages in the methods hitherto used when applied to low-grade ores, and describes improved methods of both volumetric and gravimetric analysis, perfected in the laboratories of the Bureau of Mines, that are more rapid and accurate than any previously devised. Also, comparison is made of the two methods, as regards their application and relative advantages.

The Properties of Some Stoneware Clays. H. G. Schurecht. Technical Paper 233. 41 pp. Paper, 10 cents. 1920. In connection with its investigations having to do with the utilization of high-grade clays in the United States, the Bureau of Mines has conducted, in coöperation with the Ohio Geological Survey, a study of the properties of some Ohio and Pennsylvania stoneware clays. The investigation had special reference to the possible use of these clays in making chemical stoneware, but many of the results brought out can be applied to a number of other ceramic industries.

BUREAU OF STANDARDS

Lime: Its Properties and Uses. Circular 30, 2nd edition. July 6, 1920. 25 pp. Paper, 5 cents.

Recommended Specifications for Green Paint—Semipaste and Ready-Mixed. Prepared and recommended by the United States Interdepartmental Committee on Paint Specification Standardization, June 28, 1920. Circular 97. 10 pp. Issued August 23, 1920. Specifications are outlined for the pigment, liquid, semipaste, and ready-mixed paint; and methods of sampling, laboratory examination of the semipaste, analysis of the pigment, laboratory examination of the mixed paint, and the reagents employed are described.

Measurement of Plasticity of Mortars and Plasters. W. E. Emley. Technologic Paper 169. 27 pp. Paper, 10 cents. 1920. Attention is directed to the enormous influence which the degree of plasticity has on the economic use of these materials. An instrument has been devised that will measure plasticity. Another instrument is now being built which is much simpler in design and on a much larger scale than the present instrument. It is proposed to use this new plasticimeter to attack the problem of the plasticity of concrete. The instrument is available for use in writing specifications for lime and gypsum.

DEPARTMENT OF AGRICULTURE

A Modified Boerner Sampler. E. G. BOERNER. Department Bulletin 857. 8 pp. Paper, 5 cents. Of interest to grain dealers and laboratory workers engaged in testing grain.

Pickering Sprays. F. C. COOK. Department Bulletin 866. 47 pp. Paper, 10 cents. Issued August 24, 1920.

Atmospheric Nitrogen for Fertilizers. R. O. E. DAVIS. Separate No. 803 from Yearbook of the Department of Agriculture, 1919. 7 pp. Paper, 5 cents.

COMMERCE REPORTS—AUGUST 1920

Domestic sales of **potash** have come to a complete standstill in Germany. (P. 612)

Oil is being used quite extensively as **fuel** in the Danish industrial plants. (P. 639)

The embargo on the exportation of **hides and leather** from Australia has been removed. (P. 641)

There is said to be a market for American **copper** in Manchuria. (P. 664)

The exportation from New Zealand of **kauri gum** that has been adulterated or mixed with other gum is prohibited. (Pp. 666–7)

A modification, increasing the import duties on **coal-tar dyes**, has been made in Spain. (P. 667)

The **tanning** industry in Spain is reviewed. (Pp. 677–9)

The rapid decrease in the output of **gold** in Australia continues. (P. 680)

The **salt** reserves in the Crimea are said to be unlimited. Large quantities of **sulfate of soda** and of **bromine** also are obtained, as well as substances for the production of high-grade cement. (P. 682)

The **vegetable oil industry** of Ceylon is flourishing, and in 1919 the United States received all of the **citronella oil**, 992,850 lbs., exported therefrom. (Pp. 698–9)

The **dyestuffs** trade in Japan is reviewed. (P. 710)

A corporation has been formed in London for placing in Spanish ports stocks of **mineral oils.** (P. 715)

Regulations governing the importation and sale of **chemical fertilizers** in Brazil are now in force. (P. 728)

Germany has revised her **export duties** on the *ad valorem* system and the new duties are given on hides and skins, products of oil mills, of the starch industry, mineral and fossilized raw materials, waxes, chemical and pharmaceutical products, leather, rubber goods, and metals. (Pp. 729–30)

It is now possible to purchase **purple ore** in Bordeaux. (Pp. 753–4)

The State of Sonora has planned to establish in Nogales, Sonora, a permanent exhibit of **agricultural, mining,** and industrial products of the state. (P. 759)

The **spelter** industry in South Wales has experienced a steady decline since the close of hostilities. (P. 764)

Fuel oil bunkering stations are being established in Australia, as the principal steamship lines trading there have decided to use oil instead of coal fuel. (P. 770)

Japanese authorities have decided to discontinue the allotment of **crude camphor** to camphor refiners in the United States and other countries foreign to Japan. The authorities have, however, decided to allot to refiners in the United States, at a special discount, 15,000 lbs. of refined camphor a month. (P. 783)

The **manganese** industry of Japan is reviewed. (P. 791)

The use of **peat** as fuel on Swedish railways so far shows favorable results. (P. 793)

Negotiations are pending between Germany and France with the object of coming to an agreement with respect to the Alsatian potash industry (P. 802)

Papyrus in the Congo is to be exploited. It has been shown on analysis to contain 37.8 per cent of cellulose. After research and experiments, a process was discovered for bleaching the plants which had been vainly sought for 50 years. (P. 802)

The resumption of the German **chemical** trade is dependent upon the supply of coal. (Pp. 807–11)

The government of Manitoba is taking steps to construct a railway into the Manitoba mineral belt with a view to the exploitation of its **mineral resources.** (P. 827)

The prices for **camphor** in Foochow at present are unusually low, there are fairly good stocks on hand, and local firms are anxious and ready to do business with the United States. (Pp 835–7)

The Italian **pumice** industry is reviewed. (Pp. 839–40)

The final estimate of India's 1919–20 **oil seed** crop is given as 1,174,000 long tons for rape and mustard and 433,000 long tons for linseed—an increase of 54 per cent for the former and 84 per cent for the latter. (Pp. 849–50)

Statistics are given showing the production, importation, and exportation of **fats and oils** in the United States for the three-month period ended June 30, 1920. (P. 851)

There appears to be a potential market for American **dyes** in Foochow. (P. 870)

The following table gives the output of Mexican **mines** during 1916, 1917, 1918, and 1919 (January to September), quantities being stated in kilos of 2,204 lbs. each:

METALS	1916 Kilos	1917 Kilos	1918 Kilos	1919 Kilos
Gold	11,748	23,543	25,313	22,944
Silver	926,142	1,305,988	1,944,542	1,949,673
Copper	28,411,248	50,985,923	70,223,454	50,893,612
Lead	19,970,986	64 124,752	98 837,154	67,378,353
Zinc	37,449,226	14,757,333	20,698,995	8,665,413
Antimony	828,767	2,646,544	3,268,546	627,704
Tin	292	9,214	13,537	2,117
Tungsten	12,250	187,637	149,486	29,292
Molyhdenum	......	......	27,371	2,356
Manganese	......	73,387	2,878,383	2,849,979
Mercury	......	33,132	163,598	113,865
Arsenic	......	1,284,820	1,881,011	2,188,333
Amorphous graphite	470,343	420,046	6,190,819	5,011,619

(P. 883)

The president of the government Board of Trade has declared that the **dye-making** industry in the United Kingdom is regarded as a military necessity, and has pledged the government to bring in legislation which would make it possible thereafter to import synthetic dyestuffs under license only. (Pp. 884–5)

A concession has been granted for the extraction of **oil of liquid amber** in Honduras. (P. 887)

An American has secured a concession for the establishment of a **shark oil** industry in the Gulf of Fonseca. (P. 887)

Statistics relative to the **vegetable oil** supplies of the United Kingdom for the first six months of 1920 show that the imports of oil seeds, oil nuts, etc., from abroad were in the aggregate much in excess of the same period of last year and fast approaching pre-war level. A significant fact is the very considerable increase in the United Kingdom exports of refined oil, 10,161 tons, against only 632 tons in the same period last year, and the substantial reduction in the imports of refined oil from abroad, 23,717 tons, against 51,760 tons. Imports of refined cottonseed oil fell to 1,116 tons, compared with 20,785 tons a year ago (P. 915)

The restriction on the importation of foreign **dyestuffs** into Jamaica has been suspended temporarily. (P. 929)

An **oil well** has been discovered at Kosenpo, Formosa, delivering oil of a very good quality at the rate of 1,700 gallons per day. (P. 940)

American chemical products are now well established in Japan, but whether they will be able to hold this trade will depend upon the maintenance of a high quality of goods at competitive prices. (Pp. 940–1)

An oil company has been organized in Rumania which will be under the control of the state, and all forms of petroleum products necessary for home consumption will be distributed by the state by means of the new company under the Ministry of Industry and Commerce. (P. 950)

It is suggested that the most profitable way of utilizing the Bassia flowers in India would be as a source of a mixed **motor spirit** of the "natalie" type for local use. That motor spirit can be produced on a manufacturing scale from Bassia flowers has already been demonstrated. (Pp. 953–4)

The Canadian **pulp** and **paper** industry is reviewed. (Pp. 968–9)

Important developments are anticipated in connection with the Tasmanian iron ore deposits. (P. 970)

A company has been formed to exploit the large **salt** deposits in South Australia for the purpose of manufacturing caustic soda and chlorine. (P. 971)

Requirements for the importation of **synthetic dyestuffs** into Persia are given. (P. 982)

The exportation from France of refined and unrefined **methanol** and **acetone** has been prohibited. (P. 993)

The demand for **sulfate of ammonia** in the Dutch East Indies is great and the present opportunity for the United States to gain a permanent hold on this trade is eminent. (Pp. 996–7)

Pulverized **lignite** is being used for fuel in Australia. (P. 1007)

Manganese ore is available for export from Argentina (P. 1007)

SPECIAL SUPPLEMENTS ISSUED IN AUGUST

PARAGUAY—48*a*
PERU—49*a*
CHINA—55*c*
JAPAN—58*b*
AUSTRALIA—63*a*
ALGERIA—66*a*

STATISTICS OF EXPORTS TO THE UNITED STATES

BAHAI—(P. 847)
Chrome
Manganese
Rubber
Wax

FERNIE—(P. 734)
Copper
Fluorspar
Lead ore
Zinc ore

HANKOW—(P. 1032)
Antimony
Cottonseed oil
Rape-seed oil
Sesame-seed oil
Wood oil
Carbonate of potash
Sulfate of potash
Tallow

LONDON—(P. 1027)
Rubber
Drugs and chemicals
Tin
Nitrogenous fertilizer
Creosote oil
Aluminium
Gums
Dynamite glycerol

HONGKONG—(P. 685)
Antimony
Camphor
Chemicals

ERITREA—(P. 647)
Gasoline
Gum arabic
Naphthalene
Paints
Potash

GREAT BRITAIN—(P. 742)
Tin plate
Black plate

MALAGA—(P. 699)
Tartar (crude)
Thymol
Grease and oils
Sulfur oil
Essential oils
Vegetable oils
Oxide of iron
Ocher

PERU—(P. 818)
Rubber

BRAZIL—(P. 818)
Rubber

BOOK REVIEWS

Explosives. By E. B. BARNETT. xv + 241 pp. D. Van Nostrand Co., New York, 1919. Price, $5.00 net.

This book, as stated in the preface, is designed to "give a clear but concise account of the manufacture of explosives, together with an outline of the methods used for investigating this class of substances," and this is quite satisfactorily accomplished. Owing to the conciseness of the work it was naturally impossible to go into details, but the whole field of explosives is covered in a general way. Especial attention is paid to safety coal-mine explosives, called permissible explosives in this country, and considerable space is given to methods of testing explosives, with some discussion of the theories on which the tests are based.

The principal objection to the book for the use of American readers is that it is based on English practice, which differs materially from the American in this subject. This is particularly noticeable in the remarks on nitrostarch, page 62 in which it is stated that nitrostarch has not been successfully manufactured and used in explosives. As a matter of fact, nitrostarch explosives have been used in this country for many years, and millions of pounds of these explosives have been manufactured.

There are a few minor errors, as is the case with practically every book published. For instance, the melting point of pure trinitrotoluene is given on page 56 as 81.9° C., whereas it has been determined by several independent investigators as 80.6–80.8°, and is so given in C. A. Marshall's large work on "Explosives," to which the author acknowledges his indebtedness.

ARTHUR M. COMEY

The Profession of Chemistry. By RICHARD B. PILCHER. xiv + 199 pp. D. Van Nostrand Co., New York, 1920. Price, $2.00 net.

In this little book of some two hundred pages, Mr. Pilcher gives a complete history of the development of chemistry in England from the point of view of the professional chemist. Beginning with the alchemists he describes the growth of the science, the differentiation between pharmacists and chemists, the origin of the various chemical societies and organizations of England, their aims and accomplishments, and their future possibilities. A considerable portion of the book is taken up with suggestions and advice as to the proper education and training of those who intend to take up chemistry as their profession, and repeatedly emphasizes the necessity of a broad foundation and thorough preparation in fundamentals. He thrashes out the old question of Latin requirements and reviews the arguments pro and con in a fair and judicial manner. The whole chapter on the education and training of chemists is sound.

While the book deals entirely with chemistry as practiced in England, and considerable of the space is devoted to description of the organization and duties of such societies as the Institute of Chemistry, the Society of Public Analysts, and others, the problems discussed are identical with those that exist in the United States, and the conclusions reached are the same. The importance of chemistry to civilization, the part played by chemistry in the welfare of the nation, the wonderful future promised, are truths, and truth is not confined to one section of the world. With the transposition of a few names, the volume might have been issued as an American publication, and would have had the endorsement of the majority of American chemists.

The book is written in a most delightful style and bears the evidence of first-hand knowledge. A great amount of information is presented in a clear and compact form. It should be read by every American chemist, partly as giving a vivid picture of chemistry and chemists in England, but mainly as a presentation of the problems of chemists in general, and common-sense methods of solving them.

EDMOND O'NEILL

Standards and Tests for Reagent Chemicals. By BENJAMIN L. MURRAY. x + 385 pp. D. Van Nostrand Co., New York, 1920. Price, $3.00 net.

It would be impossible to write a book on this subject which did not continue the series from the original Krauch to the 1914 translation of Merck. The present work has, however, enough new features to entitle it to consideration as much more than a mere revision of former books.

The descriptions of the chemicals are more complete, especially as to their uses. Information in regard to proper containers and conditions of storage, and warnings of the dangerous or unpleasant properties of many substances will prove valuable to chemists without wide experience along these lines.

The properties given are those of high-grade commercial reagent chemicals. Constants like boiling and melting points are on this basis, with results which have been reported for specially purified laboratory specimens stated as "theory," as under picric acid: "it melts between 121° and 123° C. (theory 122.5° C.)."

Practically all the tests for strength and purity have been established by long use. Those for special reagents follow the authoritative procedures published by the authors, institutions, and societies responsible for the standards. Some time-honored statements of standards for strength and purity have been changed to agree better with the facts, although further reduction might be advisable for some reagents like hydrochloric and sulfuric acids, which have been reduced from 37 and 95 per cent, respectively, to 36 and 94 per cent. The frequent use of 0.0000 per cent to mean failure to respond to the test for an impurity may be misleading, though it is stated: "The percentage figures in which the above limits are stated were in part determined by the customary quantitative tests, and to this extent are accurate; in part by qualitative tests in which the reactions in unknowns are compared with those in knowns. Such comparative tests have a real value in determining the usefulness of reagents, although they should not be regarded as exact. The tests will insure good reagents even though the stated percentages of impurities may not be entirely correct."

About 300 items are discussed, of which 40 are variations of others, such as solutions, different strengths of acids, or preparations for special purposes. More indicators are listed than in the former works. Potassium phosphate monobasic and sodium phosphate dibasic for use in measurement of hydrogen-ion concentration are tested according to the directions of Sorenson. Other newer reagents take the place of those less used which are omitted from former lists.

The following useful tables are included: Atomic weights (1918); calculation of acetic anhydride and acid from titrations of mixtures; congealing points of acetic acid of strengths from 98.00 to 100.00 per cent; percentages corresponding to specific gravities at 60°/60° F. for hydrochloric, nitric, and sulfuric acids, and ammonia; composition of fuming sulfuric acid corresponding to different percentages of total SO_3; specific gravity at 15°/15° C. for methyl alcohol of various percentages by volume.

The statement that the limits for impurities are "maxima permissible in chemicals for miscellaneous reagent purposes," and the corresponding principle in regard to strength should be kept in mind if the standards given are to be used in making purchases. For certain uses reagents of greater strength or purity can and must be obtained. W. D. Collins

Treatise on General and Industrial Inorganic Chemistry. By Dr. Ettore Molinari, Professor of Industrial Chemistry at the Royal Milan Polytechnic. 2nd Edition, translated from the fourth revised and amplified Italian edition by Thomas H. Pope, B.Sc., F.I.C., A.C.G.I. xix + 876 pp., 328 illustrations + 2 phototype plates. P. Blakiston's Son & Co., Philadelphia, 1920. Price, $12.00.

The third edition of this chemistry, translated by Dr. Ernest Feilmann, appeared in 1913 and constituted the first English edition. This translation of the fourth edition by Pope constitutes the second English edition. Nearly 200 pages have been added. The war experiences of the author lead him to make the following remarks in the preface:

> The problem of the war, which in all countries has proved to be eminently chemical in character, shows how much the governments of certain nations are to blame for their past neglect of the development of the teaching of chemistry and of its modern applications. At the same time their fault would be none the less grave if their present experiences cause them to regard our science merely as an instrument for the preparation of monstrous devices destined to the work of destruction and carnage.
>
> When mankind, which is paying with its blood for the criminal follies of the ruling classes, ceases to be deceived by the attractive, idealistic veneer masking the true fundamental ends of every war, then will chemistry no longer be a tool of barbarism, but will direct its wonderful activity to the improvement of the material and intellectual welfare of man throughout the world, irrespective of race.

The book at first reminds one of Bloxam's well-known chemistry, so near are the two alike in mechanical details and in much of the subject matter. The difference lies mainly in the fact that the space devoted to organic chemistry in Bloxam is given to industrial chemistry in Molinari.

Molinari divides his book into three general parts: Part I embraces 111 pages, dealing with the laws of matter, chemical equations, solutions, and allied topics of a general nature. In Part II, 374 pages are given to a discussion of the non-metals and their compounds. The remainder of the book (Part III) is devoted to a study of the metals, following the general order of arrangement in the periodic table.

The book is distinctive in that it deals with both inorganic and industrial chemistry. Following the discussion of most of the elements and their important compounds, there is given a rather extended discussion of the commercial methods of preparation, often including statistics of production and cost of finished product. Unfortunately for the American student, the cost is given in the English system of coinage. It is a question whether or not it is advisable to attempt to give costs of various chemicals in such a treatise, especially at the present time when costs are so "out of joint." Nevertheless, the book serves to give approximate costs with some degree of accuracy, and it is advisable for a student to know whether, say, a pound of sulfuric acid is worth five cents or one dollar, and that is more than many of them do know—at least until they settle up their laboratory accounts. It is of interest to note that the Italian government paid as high as $10.00 a gram for platinum during the war.

It goes without saying that a book which attempts to be a treatise on both inorganic chemistry and industrial chemistry is likely to be unsatisfactory from either standpoint. Moreover, a book written on industrial chemistry by an Italian author is not likely to be extremely accurate from the standpoint of methods used in the United States. Accordingly, it is not difficult to find minor misstatements as to our practices. Nevertheless, the author has succeeded in bringing together into one easily handled, compact volume a vast amount of information of value to chemists. The reviewer has had the volume on his desk for some time and has found himself constantly turning to it for certain facts. It is hardly adapted as a textbook to our American needs, but it will find a place as a compact, handy reference book. William McPherson

Annual Reports of the Society of Chemical Industry on the Progress of Applied Chemistry. Issued by the Society of Chemical Industry. Volume IV, 1919. 632 pp. Society of Chemical Industry, Central House, 46–47 Finsbury Square, London, E. C. 2, England, 1920. Price, to members, 5s. 6d.; non-members, 12s. 6d.

The various sections of these *Reports* now cover the entire range of subjects dealt with in the *Journal of the Society of Chemical Industry* in its industrial reviews, transactions, and abstracts, namely, plant and machinery; fuel; gas, destructive distillation, and tar products; mineral oils; coloring matters and dyes; fibers, textiles, cellulose, and paper; bleaching, dyeing, printing, and finishing; acids, alkalies, salts, etc.; glass; refractories; ceramics and building materials; iron and steel; metallurgy of the non-ferrous metals; electrochemistry; oils, fats, and waxes; paints, pigments, varnishes, and resins; India rubber; leather and glue; agricultural chemistry; sugars, starches, and gums; fermentation industries; foods; water and sewage purification; fine chemicals, medicinal substances, and essential oils; photographic materials and processes; explosives; and analytical chemistry. The reports on explosives (1914–1919) and on technochemical analysis appear for the first time; and the reports on ceramics and building materials, and on the fermentation industries for 1918, held over from Volume III, are also included, together with the reports on these subjects for 1919. In each of the 28 reports contained in Volume IV, the patent and journal literatures are critically reviewed by an expert, and each report serves as a concise resumé of the technical progress made during 1919 in the specific field to which it relates.

The period covered by these *Reports* was typically transitional: its outstanding feature was the transference of industry from war-time to peace conditions. In certain fields of chemical manufacture—especially in the "key" industries—technical difficulties were overshadowed by the continuous disagreements in the adjustment of affairs between different groups connected with the industries; but notwithstanding this necessary attention to economic considerations, the scientific progress made generally was very real. Then, too, technical matters of interest are contained in the reports of the enormous developments which resulted during and from four years of war.

This convenient, well-indexed, and authoritative compend constitutes a digest of the literature of industrial chemistry for the year 1919. The volume and its three foregoing companions should be in the library of every chemist or chemical engineer who reads much, but not many words. Summaries of this type, properly used, induce creative reading and furnish materials for research. W. A. Hamor

Standard Methods for the Examination of Water and Sewage. 4th Edition. vii + 115 pp. American Public Health Association, Boston, 1920. Price, $1.25 (waterproof cloth); $0.60 (flexible paper cover).

The present edition is practically a reprinting of the third edition of this standard work. No changes whatever have been made in the portion of the book devoted to chemical methods of analysis, even the numbering of the pages remaining the same. In the bacteriological section the changes are comparatively slight. Witte's peptone is no longer the standard, improvements in American brands, aided by war conditions, having replaced it by the domestic product. The only important changes in procedure consist in a modification of the method of testing the reaction of media by adjusting them to a somewhat precise hydrogen-ion concentration through the use of phenol red, a slight change in the fuchsin-sulfite reagent for Endo's medium, and the introduction of a synthetic medium for the methyl red test.

The use of thinner paper renders the volume somewhat handier to use, and, as before, it will find widespread laboratory application, as representing in official form the selected methods of American water analysts. A. G. Woodman

The Organization of Industrial Scientific Research. By C. E. Kenneth Mees, D.Sc., Director of the Research Laboratory of the Eastman Kodak Company, Rochester, N. Y. 8vo. 175 pp. McGraw-Hill Book Co., Inc., New York, 1920. Price, $2.00 net.

During the past five years there has been a veritable deluge of papers and addresses dealing with the value of industrial research and its relation to manufacturing. Dr. Mees deals with such material only by title in a bibliography, passing directly to the problem of organizing and operating industrial research laboratories. Following four introductory chapters, Chapters V to VIII deal, respectively, with the internal organization, the staff, the building and equipment, and the direction of industrial research laboratories. The final chapter deals in some detail with the design of laboratories for specific industries. A classified bibliography of over 150 titles of papers dealing with research, in addition to footnote references throughout the text, adds to the value of the book as a work of reference. There are also indexes to authors and specific laboratories cited in the text.

Major differences of opinion being practically absent, this field of exposition is free from both argument and rebuttal. Each paper or address on the subject of research reflects chiefly the author's limitations in experience and in expression. It would be a great service indeed should some supermind reduce the complex mass of facts to a firm, well-ordered whole, crystal-clear, and firm. But the mass is palpably colloidal in its nature, and thus far resistant to all attempts to filter and centrifuge. Most attempts at desiccation and fusion have but resulted in oxidation to impalpable powder! Dr. Mees has shown wisdom in not attempting the impossible, he has treated a single phase of the subject with all his well-known lucidity of thought and expression. There is in no instance any doubt as to his meaning. He conveys the general impression that the general problem of organizing and operating a laboratory is a simple one.

If criticism must be offered, it should be directed perhaps (1) to the lack of discussion of some of the greatest unsolved problems in research organization, and (2) to the somewhat limited perspective of the author. Among the larger unsolved problems still under investigation is the psychological one of securing the best flow of the most valuable ideas from research men. With too great isolation, they run dry of ideas or tend to run off on tangents. With too close association there is too little continuity of effort. Periodical conferences of from four to eight men meeting about twice a month appears to be the best arrangement yet devised, but it is by no means entirely satisfactory. Another, and one of the greatest outstanding problems in large manufacturing organizations is that of properly utilizing the results of investigations. Dr. Mees mentions small-scale manufacturing as an intermediate phase in development, but this obviously does not apply to improvements in processes and materials employed on a large scale. In all large-scale manufacturing, it is usual to find the superintendents in charge quite indifferent to all but the most radical improvements. Some of the larger concerns are now experimenting with an intermediate department of internal information, close to high authority on the one hand, and in close touch with all new developments in certain fields.

Dr. Mees writes of industrial research as though it were a discrete entity appropriate to all manufacturing concerns above a certain minimum size and grade, whereas it is applicable to manufacturing of all sizes and degrees of complexity. Even a wagon factory, making but a single style and size of wagon, is concerned with the quality of the wood and iron purchased, the wearing and weathering properties of these materials, and with their heat treatment, impregnation and covering, as well as in improved machinery and methods of handling. In a larger concern in keener competition with its rivals, these functions are simply more highly differentiated, and are handled by larger corps of experts. As a rule, industrial research laboratories are not established to care for new lines of work but rather provided separate quarters when crowded out of manufacturing establishments. Objection may well be raised also to Dr. Mees' classification of laboratories into two distinct types, the "convergent" and "divergent," since laboratories exist of all intermediate diversities of field covered; it is difficult, in fact, to place his types even as extremes.

The time is not far distant, we trust, when we shall have done with experimenting on research organization and methods; when some master mind shall assemble all that is best of what is known in one master work, outlining the ideal and marshaling in united effort the combined forces of educational, industrial, engineering, and governmental organizations in logical effective research. P. G. Nutting

NEW PUBLICATIONS

Chemistry: Textbook of Chemistry for Nurses and Students of Home Economics. Annie Louise Macleod. 180 pp. Illustrated Price, $2.25. McGraw-Hill Book Co., Inc., New York.

Drugs: Practical Standardization by Chemical Assay of Organic Drugs and Galenicals. A. B. Lyons. 397 pp. Price, $3.50. Nelson, Baker & Co., Detroit, Mich.

Fuel Analysis: Technical Gas and Fuel Analysis. Alfred H. White. 2d Ed., revised and enlarged 319 pp. Price, $3.00. McGraw-Hill Book Co, Inc, New York.

Fuel Oil in Industry. Stephen O. Andros. 274 pp. Price, $3.75. The Shaw Publishing Co., Chicago, Ill.

Mésures Electrotechniques. Albert Turpain. 183 pp. 105 figs Price, 20 fr. Dunod, Paris.

Molasses: Reading List on Molasses. Compiled by Clarence J. West. Bibliographic Series No. 5. 52 pp. Arthur D. Little, Inc., Cambridge, Mass.

Nature of Animal Light. E. Newton Harvey. 182 pp. Illustrated Price, $2.50. J. B Lippincott Co., Philadelphia, Pa.

Paper: Chemistry of Pulp and Paper Making. Edwin Sutermeister 250 pp. $5^1/_2 \times 8^1/_2$. Illustrated. Price, $3.00 John Wiley & Sons, Inc., New York.

Resins: Analysis of Resins, Balsams and Gum-Resins. Karl Dieterich. Translated from the German. 2d English Ed., revised and enlarged. 432 pp. Price, 17s. 6d. net Scott, Greenwood & Son, London.

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Concrete: Soaking Concrete in Magnesium Fluosilicate and Sodium Silicate Solutions *Concrete*, Vol. 17 (1920) No 1, p. 28–29.

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MARKET REPORT—SEPTEMBER, 1920

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

		Sept. 1	Sept. 15
Acid, Boric, cryst., bbls.	lb.	.18	.18
Hydrochloric, com'l, 22°	lb.	.03¼	.03¼
Hydriodic	oz.	.19	.19
Nitric, 42°	lb.	.08½	.08½
Phosphoric, 50% tech.	lb.	.25	.25
Sulfuric, C. P.	lb.	.07	.07
Chamber, 66°	ton	22.00	22.00
Oleum	ton	25.00	25.00
Alum, ammonia, lump	lb.	.04¼	.04¾
Aluminium Sulfate (iron-free)	lb.	.05½	.05½
Ammonium Carbonate, pwd.	lb.	.16	.16
Ammonium Chloride, gran.	lb.	.15	.15
Ammonia Water, carboys, 26°	lb.	.11	.11
Arsenic, white	lb.	.14	.14
Barium Chloride	ton	140.00	140.00
Nitrate	lb.	.11	.11
Barytes, white	ton	30.00	30.00
Bleaching Powd., 35%, Works,	100 lbs.	6.50	7.00
Borax, cryst., bbls.	lb.	.10	.10
Bromine, tech.	lb.	.75	.75
Calcium Chloride, fused	ton	33.00	33.50
Chalk, precipitated, light	lb.	.05	.05
China Clay, imported	ton	18.00	18.00
Copper Sulfate	100 lbs.	8.25	8.25
Feldspar	ton	8.00	8.00
Fuller's Earth	100 lbs.	1.00	1.00
Iodine, resublimed	lb.	4.35	4.35
Lead Acetate, white crystals	lb	.16	.13
Nitrate	lb	.15	.15
Red American	100 lbs.	.12¼	.12¼
White American	100 lbs	.10½	.10½
Lime Acetate	100 lbs	3.50	3.50
Lithium Carbonate	lb	1.50	1.50
Magnesium Carbonate, Tech.	lb.	.13	.13
Magnesite	ton	65.00	65.00
Mercury flask	75 lbs.	75.00	75.00
Phosphorus, yellow	lb.	.35	.35
Plaster of Paris	100 lbs	1.50	1.50
Potassium Bichromate	lb.	.32	.34
Bromide, Cryst.	lb	.75	.75
Carbonate, calc., 80–85%	lb	.18	.20
Chlorate, cryst.	lb.	.16	.18
Cyanide, bulk, 98–99%	lb	.50	.50
Hydroxide, 88–92%	lb.	.23	.28
Iodide, bulk	lb.	3.35	3.35
Nitrate	lb	.15	.15
Permanganate, U. S. P.	lb.	.75	.75
Salt Cake	ton	Nominal	Nominal
Silver Nitrate	oz.	.62	.61
Soapstone, in bags	ton	12.00	12.00
Soda Ash, 58%, bags	100 lbs	3.00	2.75
Caustic, 76%	100 lbs.	4.80	4.40
Sodium Acetate	lb.	.12	.12
Bicarbonate	100 lbs.	3.00	3.00
Bichromate	lb.	20½	.19½
Chlorate	lb.	.10	.10
Cyanide	lb.	.50	.50
Fluoride, technical	lb.	.28	.22
Hyposulfite, bbls.	100 lbs.	4.00	4.00
Nitrate, 95%	100 lbs.	3.60	3.50
Silicate, 40°	lb	.02	.01½
Sulfide	lb.	.10¼	.10¼
Bisulfite, powdered	lb	.06½	.06½
Strontium Nitrate	lb.	.15	15
Sulfur, flowers	100 lbs.	3.75	4.00
Crude	long ton	25.00	25.00
Talc, American, white	ton	20.00	20.00
Tin Bichloride	lb	.21½	.21½
Oxide	lb	.60	60
Zinc Chloride, U. S. P.	lb	.50	.50
Oxide, bbls.	lb.	.12	12

ORGANIC CHEMICALS

		Sept. 1	Sept. 15
Acetanilide	lb.	.60	.65
Acid, Acetic, 28 p. c.	100 lbs.	4.00	3.75
Glacial	lb	.12	.12
Acetylsalicylic	lb.	.88	.88
Benzoic, U. S. P., ex-toluene	lb.	.85	.85
Carbolic, cryst., U. S. P., drs.	lb.	.15	15
50- to 110-lb. tins	lb	.23	24
Acid (*Concluded*)			
Citric, crystals, bbls.	lb.	.72	.67
Oxalic, cryst., bbls.	lb.	.50	.38
Pyrogallic, resublimed	lb.	2.35	2.35
Salicylic, bulk, U. S. P.	lb.	.50	.45
Tartaric, crystals, U. S. P.	lb.	.70	.65
Trichloroacetic, U. S. P.	lb.	4.40	4.40
Acetone, drums	lb.	.22	.22
Alcohol, denatured, 190 proof	gal.	1.13	1.13
Ethyl, 190 proof	gal.	7.00	7.00
Wood, Pure	gal	4.40	4.40
Amyl Acetate	gal	4.00	4.00
Camphor, Jap. refined	lb.	1.35	1.32½
Carbon Bisulfide	lb.	.08	.08
Tetrachloride	lb.	.14½	.14½
Chloroform, U. S. P.	lb.	.40	.40
Creosote, U. S. P.	lb	.70	.70
Cresol, U. S. P.	lb	.18	.18
Dextrin, corn	lb.	.07¼	.06½
Imported Potato	lb.	.12	.12
Ether, U. S. P., conc., 100 lbs.	lb.	.24	.24
Formaldehyde	lb.	.48	.44
Glycerol, dynamite, drums	lb.	.28	.28
Pyridine	gal	2.75	2.75
Starch, corn	100 lbs.	5.12	4.73
Potato, Jap.	lb.	.06½	.06½
Rice	lb	.25	.25
Sago	lb.	.05	.05

OILS, WAXES, ETC.

		Sept. 1	Sept. 15
Beeswax, pure, white	lb.	.60	60
Black Mineral Oil, 29 gravity	gal.	.22	.22
Castor Oil, No. 3	lb.	16	.16
Ceresin, yellow	lb	.16	.16
Corn Oil, crude	lb.	08½	.08½
Cottonseed Oil, crude, f. o. b. mill	lb.	.10	.10
Menhaden Oil, crude (southern)	gal	.55	.55
Neat's-foot Oil, 20°	gal.	1.65	1.65
Paraffin, 128–130 m. p., ref.	lb.	.11½	.11½
Paraffin Oil, high viscosity	gal.	.45	.45
Rosin, "F" Grade, 280 lbs.	bbl.	15.25	13.90
Rosin Oil, first run	gal.	.78	.74
Shellac, T. N.	lb.	1.10	1.05
Spermaceti, cake	lb.	.30	.30
Sperm Oil, bleached winter, 38°	gal.	1.85	1.85
Stearic Acid, double-pressed	lb.	.22½	.19½
Tallow Oil, acidless	gal.	1.25	1.25
Tar Oil, distilled	gal.	.60	.60
Turpentine, spirits of	gal.	1.55	1.49

METALS

		Sept. 1	Sept. 15
Aluminium, No. 1, ingots	lb.	.32	32
Antimony, ordinary	100 lbs.	7.50	7.25
Bismuth	lb.	2.72	2.72
Copper, electrolytic	lb.	.19	.18¾
Lake	lb.	.18¾	.18¾
Lead, N. Y.	lb.	.08¾	.08½
Nickel, electrolytic	lb.	.45	.45
Platinum, refined, soft	oz.	95.00	115.00
Quicksilver, flask	75 lbs. ea.	75.00	75.00
Silver	oz.	1.00	1.00
Tin	lb.	.47½	.45½
Tungsten Wolframite	per unit	6.50	6.50
Zinc, N. Y.	100 lbs.	8.40	8.15

FERTILIZER MATERIALS

		Sept. 1	Sept. 15
Ammonium Sulfate	100 lbs	5.35	5.35
Blood, dried, f. o. b. N. Y.	unit	8.00	8.00
Bone, 3 and 50, ground, raw	ton	48.00	48.00
Calcium Cyanamide, unit of Ammonia		4.00	4.00
Fish Scrap, domestic, dried, f. o. b. works	unit	7.25	7.25
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%	ton	6.85	6.85
Tennessee, 78–80%	ton	11.00	11.00
Potassium Muriate, 80%	unit	2.40	2.25
Pyrites, furnace size, imported	unit	18	18
Tankage, high-grade, f. o. b. Chicago	unit	7.75	7.75

COAL-TAR CHEMICALS

Crudes

		Sept. 1	Sept. 15
Benzene, C. P	gal.	.30	.30
Cresol, U. S. P	lb.	.18	.18
Naphthalene, flake	lb.	.16½	.14
Phenol, drums	lb	.15	.15
Toluene, 90%	gal	.35	.35
Xylene, 2 deg. dist. range	gal.	60	.60

Intermediates

		Sept. 1	Sept. 15
Acids:			
Anthranilic	lb.	2.20	2.20
B	lb	2 25	2.25
Benzoic	lb.	.80	.80
Broenner's	lb	1.75	1.75
Cleves	lb	2.00	2.00
Cresylic, 97–99%	gal.	1.20	1.20
Gamma	lb.	5.75	5 75
H	lb.	2.00	1.90
Metanilic	lb.	1.70	1.70
Monosulfonic F	lb.	3.50	3.50
Napthionic, crude	lb	.85	85
Nevile & Winther's	lb.	1.90	1.90
Phthalic	lb.	.60	.60
Picric	lb.	.25	.25
Sulfanilic	lb.	.37	.37
Tobias	lb.	2.25	2.25
Amino Azo Benzene	lb.	1.15	1.15
Aniline Oil	lb	.27½	.27½
For Red	lb.	.65	.65
Aniline Salt	lb.	.33	.33
Anthracene, 80–85%	lb.	.75	75
Anthraquinone	lb.	4.50	4 50
Benzaldehyde, tech	lb.	.65	.65
U. S. P	lb	1.00	1.00
Benzidine Base	lb.	1.25	1 25
Benzidine Sulfate	lb.	1.05	1.05
Diaminophenol	lb.	6.00	6 00
Dianisidine	lb.	9.00	9.00
p-Dichlorobenzene	lb.	.10	.10
Diethylaniline	lb.	1.65	1.65
Dimethylaniline	lb.	.80	.95
Dinitrobenzene	lb.	.36	.36
Dinitrotoluene	lb.	.43	.43
Diphenylamine	lb.	.80	.80
G Salt	lb	.90	.90
Hydroquinol	lb.	2.25	2.25
Metol (Rhodol)	lb	6.75	6.75
Monochlorobenzene	lb.	.15	.15
Monoethylaniline	lb.	2.15	2.15
a-Naphthylamine	lb.	.50	.45
b-Naphthylamine (Sublimed)	lb.	2.25	2.25
b-Naphthol, dist	lb.	.80	.80
m-Nitroaniline	lb.	1.05	1.05
p-Nitroaniline	lb.	1.10	1.10
Nitrobenzene, crude	lb.	.14	.14
Rectified (Oil Mirbane)	lb.	.16	.16
p-Nitrophenol	lb.	.80	.80
p-Nitrosodimethylaniline	lb.	2.90	2.90
o-Nitrotoluene	lb	.25	.25
p-Nitrotoluene	lb.	1.50	1.50
m-Phenylenediamine	lb.	1.45	1.45
p-Phenylenediamine	lb.	2.55	2.55
Phthalic Anhydride	lb.	.50	.50
Primuline Base	lb.	3.00	3.00
R Salt	lb.	.90	90
Resorcinol, tech	lb.	3.50	3 50
U. S. P	lb.	5.50	5.25
Schaeffer Salt	lb.	.75	.75
Sodium Naphthionate	lb.	1.10	1.10
Thiocarbanilide	lb.	.60	.60
Tolidine, Base	lb.	1.75	1.75
Toluidine, mixed	lb.	.44	.44
o-Toluidine	lb.	.33	.33
m-Toluylenediamine	lb.	1.40	1.40
p-Toluidine	lb.	1.75	1.75
Xylidene, crude	lb.	.50	.50

COAL-TAR COLORS

Acid Colors

		Sept. 1	Sept. 15
Black	lb.	1.25	1.25
Blue	lb.	3.00	3.00

Acid Colors (*Concluded*)

		Sept. 1	Sept. 15
Fuchsin	lb.	2.50	2.50
Orange III	lb.	1.00	1.00
Red	lb.	1.30	1.30
Violet 10B	lb.	6.50	6.50
Alkali Blue, domestic	lb.	5.50	5.50
Imported	lb.	8.00	8.00
Azo Carmine	lb.	4.00	4.00
Azo Yellow	lb.	2.00	2.00
Erythrosin	lb.	12.00	12.00
Indigotin, conc	lb.	3.00	3.00
Paste	lb.	1.50	1.50
Naphthol Green	lb.	1.95	1.95
Ponceau	lb.	1.25	1.25
Scarlet 2R	lb.	1.00	1.00

Direct Colors

		Sept. 1	Sept. 15
Black	lb.	1.00	1.00
Blue 2B	lb	.70	.70
Brown R.	lb.	1.65	1.65
Fast Red	lb.	3.50	3.50
Yellow	lb.	2.00	2.00
Violet, con't	lb.	2.20	2.20
Chrysaphenine, domestic	lb.	2.25	2.25
Imported	lb.	3.80	3.80
Congo Red, 4B Type	lb.	.90	.90
Primuline, domestic	lb.	3.00	3.00

Oil Colors

		Sept. 1	Sept. 15
Black	lb.	.70	.70
Blue	lb	1.65	1.65
Orange	lb.	1.40	1.40
Red III	lb	1.65	1.65
Scarlet	lb	1.75	1.75
Yellow	lb.	1.70	1.70
Nigrosine Oil, soluble	lb.	.90	.90

Sulfur Colors

		Sept. 1	Sept. 15
Black	lb.	.20	.20
Blue, domestic	lb.	.70	.70
Brown	lb.	.35	.35
Green	lb.	1.00	1.00
Yellow	lb.	.90	.90

Chrome Colors

		Sept. 1	Sept. 15
Alizarin Blue, bright	lb.	7.75	7.75
Alizarin Red, 20% Paste	lb.	1.10	1.10
Alizarin Yellow G	lb.	1.00	1.00
Chrome Black, domestic	lb.	1.25	1.25
Imported	lb.	2.20	2.20
Chrome Blue	lb.	2.50	2.50
Chrome Green, domestic	lb.	2.00	2.00
Chrome Red	lb.	2.00	2.00
Gallocyanin	lb.	3.25	3.25

Basic Colors

		Sept. 1	Sept. 15
Auramine, O, domestic	lb.	2.50	2.50
Auramine, OO	lb.	4.15	4.15
Bismarck Brown Y	lb.	.90	.90
Bismarck Brown R	lb.	1.20	1.20
Chrysoidine R	lb.	.75	.75
Chrysoidine Y	lb.	.75	.75
Green Crystals, Brilliant	lb.	6.00	6.00
Indigo, 20 p. c. paste	lb.	.85	.85
Fuchsin Crystals, domestic	lb.	6.50	6.50
Imported	lb.	12.00	12.00
Magenta Acid, domestic	lb.	4.25	4.25
Malachite Green, crystals	lb.	4.50	4.50
Methylene Blue, tech	lb	2.75	2.75
Methyl Violet 3 B	lb	3.00	3.50
Nigrosine, spts. sol	lb	.85	.85
Water sol., blue	lb.	.70	.70
Jet	lb.	.90	.90
Phosphine G., domestic	lb.	7.00	7.00
Rhodamine B. extra conc'd	lb.	40.00	40.00
Victoria Blue, base, domestic	lb	6.00	6.00
Victoria Green	lb	6.00	6.00
Victoria Red	lb.	7.00	7.00
Victoria Yellow	lb	7.00	7.00

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CONTENTS

EDITORIALS:

The Chapin Report 1042
Lying Down on the Job 1042
The Masquerading Filter Paper 1043
Substance Rather than Shadow 1043
Evolution in Alcohol Administration 1044
Notes 1044
CHEMICAL INDUSTRY AND TRADE OF SWEDEN, O. P. Hopkins 1045

CONTRIBUTIONS FROM THE CHEMICAL WARFARE SERVICE, U. S. A.:

A Method for Determining the Sulfur Monochloride Content of Mustard Gas-S_2Cl_2 Mixtures. W. A. Felsing, S. B. Arenson and F. J. Kopp 1054
Pressures Produced by the Action of Sulfur Monochloride upon β,β'-Dichloroethyl Sulfide. Thos. G. Thompson and F. J. Kopp 1056
The Solubility of β,β'-Dichloroethyl Sulfide in Petroleum Hydrocarbons and Its Purification by Extraction with These Solvents. Thos. G. Thompson and Henry Odeen 1057
Decomposition of and Pressure Developed by Mustard Gas in Steel Shell at 60° C. W. A. Felsing, H. Odeen and C. B. Peterson 1063
The Precipitation of Sulfur from Crude Mustard Gas by Means of Ammonia. W. A. Felsing and S. B. Arenson 1065
The Intersolubility of Chloropicrin and Water. Thos. G. Thompson and John H. Black 1066
Control Experiments in Chloropicrin Manufacture. I—The Effect of Varying Quantities of Lime upon the Yield of Chloropicrin. H. L. Trumbull, G. T. Sohl, W. I. Burt and S. G. Seaton 1068
Control Experiments in Chloropicrin Manufacture. II—Active Chlorine in the Sludge from the Manufacture of Chloropicrin. H. L. Trumbull, S. G. Seaton and Howard Durham 1068

ORIGINAL PAPERS:

A Study of the Reactions of Coal Sulfur in the Coking Process. Alfred R. Powell 1069
The Desulfurizing Action of Hydrogen on Coke. Alfred R. Powell 1077
Naphthalene Sulfonic Acids. I—Some Difficultly Soluble Salts of Certain Naphthalene Sulfonic Acids. Joseph A. Ambler 1081
Naphthalene Sulfonic Acids. II—A Method for the Qualitative Detection of Some of the Naphthalene Sulfonic Acids. Joseph A. Ambler and Edgar T. Wherry 1085
The Mechanism of Bating. John Arthur Wilson 1087
Inclusions and Ferrite Crystallization in Steel. II—Solubility of Inclusions. E. G. Mahin and E. H. Hartwig 1090
An Electrometric Method for Detecting Segregation of Dissolved Impurities in Steel. E. G. Mahin and R. E. Brewer 1095
Inflammability of Jets of Hydrogen and Inert Gas. P. G. Ledig 1098
The Reaction between Selenium Monochloride and Ethylene. F. H. Heath and Waldo L. Semon 1100
Note on Catalysis in the Manufacture of Ether. Hugo Schlatter 1101
The Hygroscopic Moisture of Flour Exposed to Atmospheres of Different Relative Humidity. C. H. Bailey 1102
Changes in the Polarizing Constants of Sugars during Refining. A. F. Blake 1104
Dicyanodiamide: A Rapid, Direct Method for Its Determination in Cyanamid and Mixed Fertilizers. Rolla N. Harger 1107
The Changes Taking Place in Cyanamid when Mixed with Fertilizer Materials. Rolla N. Harger 1111
Studies on the Corrosive Action of Chlorine-Treated Water. I—The Effects of Steel on the Equilibrium: $Cl_2 + H_2O \rightleftharpoons HCl + HClO$, and of Products of the Equilibrium on Steel. George L. Clark and R. B. Iseley 1116

ADDRESSES AND CONTRIBUTED ARTICLES:

Chemistry's Contribution to the Life Sciences. A. S. Loevenhart 1122
The Sugar Industry of France since the War. T. H. Murphy 1124

SCIENTIFIC SOCIETIES:

Proposed New Departures in Government Chemical Work; Grasselli Medal Award; Cleveland Meeting of the American Electrochemical Society; Calendar of Meetings 1126

NOTES AND CORRESPONDENCE:

Report of E. S. Chapin, Paris Representative of the Textile Alliance, Inc., to the Dye Advisory Committee of the State Department, September 29, 1920; Allied Chemical and Dye Corporation; "Crippling a Great Work;" Franklin Filter Paper; Platinum Theft 1130
WASHINGTON LETTER 1133
PARIS LETTER 1134
INDUSTRIAL NOTES 1134
PERSONAL NOTES 1136
GOVERNMENT PUBLICATIONS 1138
BOOK REVIEWS 1141
NEW PUBLICATIONS 1142
MARKET REPORT 1143

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EDITORIALS

THE CHAPIN REPORT

The report of Mr. E. S. Chapin, Paris representative of the Textile Alliance, Inc., published on page 1130, will prove extremely interesting reading to all who are following the disposition of German dyes under the terms of the Peace Treaty.

While the report was prepared primarily for the Textile Alliance and for the consumers and producers of dyes, its reading will repay all chemists, for it gives an exceedingly clear and concise review of the progress made in the distribution of German dyes, and points out the problems still awaiting settlement, problems which will eventuate as policies to be pursued during the next five years.

During his stay in Europe, Mr. Chapin attended all of the interallied conferences on dyes, was in frequent consultation with the leaders of the German industry, had constant access to accurate records, and was in Germany a number of times. For these reasons his report bears a stamp of authoritativeness which marks it as a most valuable contribution to the literature of this much-beclouded subject.

Aside from the explanatory sections of the report, there are three features of especial interest:

First—Mr. Chapin comments on "the change in the attitude of the Germans from apparent hostility to active coöperation with the Textile Alliance." This is simply another tribute to the efficiency, unselfishness, and fairness of that remarkable organization which has handled so large a volume of business for the Government throughout the war period, without one cent of profit or remuneration.

Second—To those who made such outcry a year or more ago that American textile interests were suffering severely from the influx of British goods dyed with German dyes unobtainable in this country, it must come as a distinct shock and doubtful relief to learn that "Great Britain had secured on the free market up to August 1 [1920] 200 tons of dyes. This should be compared with our figure of 400 tons as of September 7 [1920], plus the unknown quantity imported into the United States under license through other channels."

Third—The most illuminative section of the report is that bearing on the qualitative and quantitative output of the German dye plants from February to July of this year. In spite of the much-talked-of scarcity of coal and difficulties with labor, the output increased from ten to thirty-three and a third per cent of normal. The report adds: "while the production of the vat and alizarin type dye is increasing slowly from 228 tons in May to 261 tons in June and 272 tons in July, *the production of the type of dyes made in the United States is increasing by leaps and bounds* [italics are ours] from 2400 tons in May to 2800 tons in June and 3800 tons in July."

Squelch the Moses-Thomas opposition, Senators, and pass the dye bill in the form your Committee on Finance reported it!

LYING DOWN ON THE JOB

We have received a communication, printed in full, page 1132, from Mr. N. E. Franklin, president of the Kny-Scheerer Corporation of America, called forth by the editorial in the September issue entitled "Crippling a Great Work."

Mr. Franklin feels that some one took advantage of our good nature. Wrong, Mr. Franklin, entirely wrong. That editorial was inspired solely by a knowledge of the public hearing held in Washington (not the first hearing, but a second hearing before the full Senate Finance Committee), at which was disclosed the character of the opposition to the Bacharach bill, which places a protective duty on a number of war-born American products, among them surgical instruments. Mr. Franklin, who was treasurer of the Kny-Scheerer company, is doubtless aware of the opposition to the bill shown on that occasion by Mr. Brand, the then and now vice president of his company, as set forth in the brief filed with the Committee. He doubtless knows that Mr. Richard Kny, the then president and, we understand, now consulting director of the company, was also present.

In the light of this opposition it needed only a superficial investigation to learn that the Kny-Scheerer company had reverted entirely to the business of importing, having closed their Brooklyn plant. Mr. Franklin thinks that the general public is not interested in this. We take it as a matter of very grave public interest that the country is reverting to that condition which existed at the beginning of the war, when we were unable to supply adequate quantities of instruments not only to our civilian hospitals, but even to the very surgeons who were preparing to embark for France with our Army.

Mr. Franklin protests that his company is "owned and controlled solely by born Americans." Of course. That was the whole point of the editorial. He continues, these are "men who lent their services in many ways to their government during the recent great struggle." We do not doubt it; but we were criticizing not what they did during the great struggle, but since its close. *Nowhere in Mr. Franklin's letter is a single word of denial of any fact set forth in our editorial:* namely, that Mr. Kny, whose activities as a German propagandist had been so clearly set forth in the official report of the Alien Property Custodian, was retained by the American owners as president for at least a year; that Mr. E. S. Beck was retained as secretary (in this connection it is worthy of record that Mr. Beck is a brother-in-law of Mr. Scheerer, of the Jetter & Scheerer Co., of Tuttlingen, Germany, and is still secretary of the Kny-Scheerer Corporation of America, which is the sole agent in this country of the German company); that the manufacturing plant in Brooklyn is closed; and that the goods of this company were offered to consumers at figures 20 per cent below American prices. Nowhere in Mr. Franklin's letter is there any intimation that his company is planning to develop an American surgical instrument industry. It is a tacit acknowledgment that his concern is not interested in the task of continuing the development of American workmen skilled in this art, but prefers to make dividends by importing German wares. If this is not crippling a great work, then the term American economic independence is a hollow mockery. Meanwhile, we know that American workmen have recently vainly sought employment of the character they were engaged in before the renewal of German importations, that some manufacturers who had begun the manufacture of surgical instruments have been compelled to decrease by half the number of their employees, while others have quit the field entirely.

If the Kny-Scheerer Corporation of America is to continue merely an importing agency, if it is to do no constructive service in the development of an American industry, then it was a sad day for America when the Alien Property Custodian allowed this fine property to be sold to its present American owners. In the light of Mr. Franklin's own letter we are, to our regret, confirmed in the conviction that they have lain down on the job.

THE MASQUERADING FILTER PAPER

It seems to be the season for presidential letter writing. Here is another, duly published on page 1132,—this time from Mr. Herman A. Holz, president of Holz & Company, Inc., protesting against what he considers "erroneous statements published on page 955 of the Journal in reference to the 'Franklin Filter Papers' which caused so much unpleasantness at the recent Chemical Exposition."

Why does Mr. Holz write us and at such length? Holz & Co., Inc., were not mentioned in THIS JOURNAL, nor did they make any exhibit of Franklin filter paper. The display was made by the Rohde Laboratory Supply Company, and neither on its advertising leaflet, on the labels of the packages, nor on the boxes, was there any word as to German origin. In marked contrast stood out the exhibits of French and English papers shown at the Exposition. These bore on their respective labels *Made in Paris* or *Made in England*, without the slightest suggestion of dissemblance.

We know nothing of the "young business man" to whom Mr. Holz refers. Many complaints about the exhibition of Franklin filter papers came to us, in the capacity of Chairman of the Advisory Committee, during the latter part of Exposition Week. Confirmation of the German origin of the Franklin filter papers was given by Messrs. H. F. Coors and A. A. Campbell, who questioned the attendant in charge of the Rohde exhibit. Mr. Coors has confirmed our memory of his statements:

> "Telegram received. Conversation practically verbatim as follows: *Question:* I did not know analytical filter paper was made in America. No reply. *Question:* Is this made in America? *Answer:* No. *Question:* Where is it made? *Answer:* Germany. *Question:* Whom by? *Answer:* Schlucher and School [Schleicher and Schüll]. *Question:* Where in Germany? *Answer:* Dueren. This was followed by the attendant in charge offering to send me samples. My reply was to the effect that I would secure the paper through the regular channels.—H. F. COORS."

Mr. Campbell confirms this statement, for he writes us:

> "Upon question by Mr. Coors as to where the paper was made he [the attendant] seemed very reluctant in making the statement of it 'being made in Germany,' however, after the writer led him on, he told us that it was a product of 'S & S' of Dueren."

So it was not "S & S" after all, according to Mr. Holz. The coaching of the attendant seems to have been poorly done.

Finally, Mr. Holz naïvely says, "The reason for the change of label was only the difficult pronunciation of the manufacturer's name: Macherey, Nagel & Co." Why not have tried "M & N?" We are accustomed to abbreviations on German filter papers.

SUBSTANCE RATHER THAN SHADOW

A correspondent writes us in protest against the recent action of the Council advising local sections to refrain from joining local engineering and technical societies. He feels that "the idea of the parent Society trying to hamper such affiliations by resolutions passed is, in my mind, non-progressive and rather reactionary." He contends that "technically trained men, would they be chemists, civil engineers, mining engineers, or other men of similar qualifications, would naturally associate together for the purpose of furthering matters which they are especially able to further and making themselves, in this way, more felt in the community than they are at present."

Is not our correspondent confusing the substance and the shadow? Council action was taken because of direct reports from councilors that local sections had frequently been committed to policies directly in opposition to those of the parent Society and also to the convictions of a majority of their own members. Certainly such experiences make an uncomfortable and undesirable situation. That is the shadow.

On the other hand, no one will take issue with our correspondent on the desirability of mutual association on the part of technically trained men in any community. That is the substance. To gain this it is not necessary to effect a union of local sections of national organizations, but to bring together all the technically trained of a community in a purely local organization. This has been done very successfully in Indianapolis through the medium of the *Scientech Club*. This club, made up of professional, scientific, and technical men, seeks

1. To give the City of Indianapolis and the State of Indiana the benefit of the united scientific and technical knowledge and experience of its members.
2. To promote scientific and technical research.
3. To unify and coördinate the activities of the various scientific and technical societies of the State of Indiana.
4. To maintain a high professional standing and further acquaintance and fellowship among scientific and technical men.

The various groups of technically trained men are represented on its directorate, and committees carry on active work on city planning, rail traffic, food and nutrition, public health, fuel conservation and smoke prevention, research, professional ethics, patents, daylight saving, education, and highway traffic. The club holds monthly meetings and issues a monthly bulletin.

There is the real substance of association of local technical men for mutual benefit and the good of their community. Meanwhile the Indiana Section of the American Chemical Society continues as a prosperous organization, busy with its own special problems, unfettered and unembarrassed.

EVOLUTION IN ALCOHOL ADMINISTRATION

Alcohol, the chemical reagent, is to receive some meed of that official administrative consideration which Congress intended at the time the National Prohibition Act was passed. Since the public hearing before the Bureau of Internal Revenue last summer Commissioner Williams has been thoroughly sympathetic, but inadequate funds for the administration of the Act and the onerous work involved in enforcing the prohibition feature have made the problem difficult of solution.

According to announcement from Washington, the former Division of Technology has been replaced by a Permit Division, in charge of Dr. A. B. Adams, and an Industrial Alcohol and Chemical Division, in charge of Dr. J. M. Doran. The fact that these competent chemists, both of whom have been connected with the Bureau for several years, are to have charge of the new divisions, will inspire confidence and a desire to coöperate.

The Permit Division will have general administration of the features of Title II of the National Prohibition Act, relating to permits, bonds, etc. Strength to Dr. Adams in eradicating falsified applications for withdrawal of alcohol, and wisdom in eliminating the aggravating requirements which now beset those who are acting in good faith!

The Industrial Alcohol and Chemical Division will have jurisdiction of (1) the general administration of all the features embraced in Title III of the Act, with particular reference to tax-free alcohol, (2) the development of uses of denatured alcohol by laboratory work and research, (3) the supervision of construction and operation of industrial alcohol and denaturing plants and bonded warehouses, and control of government offices assigned thereto, (4) the laboratory examination of articles manufactured under Section 4 of Title II of the Act, and (5) the examination of samples obtained under the Harrison Narcotic Act. To Dr. Doran and his associates there is entrusted the development of a work which contains untold potentialities for our chemical industries, if carried out in a thoroughly efficient manner. It is to be hoped that Congress will provide adequate funds to insure maximum results.

The method of the evolution of this administrative change gives genuine satisfaction. The matter was presented earnestly but dispassionately by those to whom injustice was being done, and was received courteously and sympathetically by the authorities in Washington. Now the apparent difficulties have been overcome, and adjustments made which will open a new chapter in national chemical development.

NOTES

The London letter was unfortunately received too late for publication in this issue.

The Patent Office, which for some time past has been handicapped by a shortage of funds and personnel, is now in position to resume the furnishing of photostatic prints of the specifications and drawings of foreign patents.

The new chemical laboratory fever has struck New England. Dartmouth College is expending from $350,000 to $400,000 on such an addition to its campus. At Yale University plans for a new building for its Department of Chemistry are practically completed.

We must confess to having received a severe jolt, in spite of our usual optimism, when a correspondent recently wrote that he had resigned his position because "the company was engaging a *physician* to act as head of the chemical laboratory."

Chemistry is not being neglected by the Swan family. While Dr. J. N. Swan heads the department at the University of Mississippi, his three sons are in training for the profession. Stewart D. holds a du Pont Fellowship in the University of Chicago, William O. has won a similar honor at the University of Virginia, and Thomas H. holds an assistantship as a graduate student in Columbia University. That's not a "bunch" of chemists—it's a whole flock.

The success of the technical monographs now under preparation by the American Chemical Society depends on one thing—how far the heads of industrial concerns will allow their chemists to "open up." Lasting contributions to chemical literature, helpful to the entire chemical industry, should be made through these monographs. Here's hoping!

With so large a number of real specialists on explosives in government service and out of it, why did the Department of Justice call upon Walter T. Scheele for an exhaustive report on the Wall Street explosion? True, he had one receipt for an explosive mixture which he put to diabolical purpose in blowing up ships during the war, but this scarcely constitutes a claim for preëminent qualifications as an expert, especially in view of the evidence of his lack of ability as an explosives expert obtained by chemists in the government service during his internment. Suppose the Department of State should call on von Igel or von Papen to solve some of its problems!

CHEMICAL INDUSTRY AND TRADE OF SWEDEN

By O. P. Hopkins
1824 Belmont Road, Washington, D. C.

Weighing all the disadvantages of her position during the war against the advantages, it must be admitted that Sweden's industries have been greatly strengthened since 1914. She has sold her products to both belligerents at handsome profits and has received the highest returns from her shipping in spite of losses by submarines.

Sweden's sources of wealth lie in her forests, in her iron mines, in her waterpower, and in her shipping facilities. Agriculture is also of first importance, one-half the population devoting itself to that branch of industry, although agricultural products do not figure largely in the country's international trade. One-half of the land is covered with forests, and before the war the income from that source was $100,000,000 a year. Eighty per cent of the total exports are derived from forest and mine. Waterpower is so abundant and cheap that electric current is the power used for more than half of the manufactured products of the country. It is estimated that the potential waterpower is 6,000,000 turbine horsepower, of which something more than 1,000,000 horsepower is now utilized.

Sweden has never occupied the place in the estimation of American business men that its wealth and good will toward America deserve. More attention has been given to Swedish facilities for handling trade between America and other countries than to its own trade. During the war, however, the United States entered into closer and more extensive business relations. American goods are very well liked, and the old good will toward America, the natural result of having so many sons living and prospering in this country, has not been altered.

FOREST PRODUCTS

Swedish forest products have a world-wide reputation. The timber is sold in many markets, often in competition with the American article, and while some varieties are admittedly inferior to corresponding American timber in quality, this is more than offset in many cases by the care with which it is prepared to meet the requirements of the foreign buyer.

The wood pulp manufactured in Sweden has a deservedly high reputation everywhere and is produced to the extent of considerably more than a million tons a year, of which the finest chemical pulp is largely exported, while much of the cheaper pulp is manufactured into paper in the country. The difficulty of getting sulfur during the war had a depressing effect on the chemical-pulp industry, although some of the plants managed to get along with Norwegian pyrites. The pre-war importation of sulfur was about 40,000 tons a year, the principal source of supply being Italy. Considerable quantities have since been obtained from the United States.

Some 350,000 tons of paper and cardboard are produced in Sweden annually, and the newspapers of Europe are pretty much dependent upon this source of supply. The finest grades of paper are imported.

Wood-distillation products are an important factor in any consideration of the Swedish chemical industry. In the order of quantity produced, these products are tar and tar oil, rosin, turpentine, acetate of lime, pitch and pitch oil, methanol, formalin, wood oil, and creosote. Charcoal is still used extensively in iron smelting, but most of it is made in kilns rather than ovens.

Rapid strides have recently been made in the manufacture of spirits from the residual lye of the sulfite-pulp factories. It is estimated that the potential yield from the residue now available is not less than 36,000,000 liters of 100 per cent spirits a year. The actual production is said to be about 12,000,000 liters.

PRODUCTION OF METALS

The Swedish iron and steel industry is not in the front rank in point of quantity produced, but for quality its reputation is unexcelled. The ores are of excellent quality, and the smelting, formerly with charcoal and latterly largely with electric current, has given to the world a wonderfully fine iron. The increasing use of electricity in the manufacture of steel has also set a high standard in that line. Swedish steel is liked in this country for safety-razor blades, and Swedish ball bearings find their way into all countries. The production of iron ore totals some 7,000,000 tons a year, and makes up more than 95 per cent of the metalliferous ores mined.

The production of ferro-alloys is important, and has kept pace with the growth of the steel industry.

A war development was the revival of copper production, which once was an important feature of Swedish industry. It is not expected that the industry will grow to large proportions, but it is likely that the success of electrolytic refining of copper will insure the continuance of a domestic supply of refined copper.

ELECTROCHEMICAL INDUSTRY

Hydroelectric power has not been developed in Sweden on quite so grand a scale as in Norway, nor is it used in the same proportions for the various industries, but it is a mighty factor in the country's prosperity. As in Norway, the development has taken place to offset the lack of coal. In the electrochemical industry, the chief use of current is for the manufacture of pig iron, ferro-alloys, and calcium carbide. The fixation of atmospheric nitrogen is comparatively unimportant when the extent of this industry in Norway is recalled.

Arranged in the order of power used, the various Swedish electrochemical industries are as follows: Pig iron, 90,000 horsepower; ferro-alloys, 60,000 horsepower; calcium carbide, 40,000 horsepower; atmospheric nitrogen, 16,000 horsepower; steel, 10,000 horsepower; caustic soda and bleaching powder, 3,000 horsepower; potash salts, 2,700 horsepower; graphite, 2,000 horsepower; phosphorus, 1,500 horsepower. The figures are estimates for 1918.

As in other countries where waterpower is available, the development of hydroelectric plants was greatly stimulated by the war.

FERTILIZERS

Although the agricultural products of Sweden do not enter largely into international trade, the fact remains that half the population is engaged in farming, and fertilizers are an important item in the Swedish chemical market.

Before the war there were heavy importations of the following artificial fertilizers, in the order of quantity: potash salts, from Germany; raw phosphate, from the United States, England, Germany, Australia, and Tunis; sodium nitrate, originating in Chile, but imported from Germany; Thomas phosphate and slag, from England and Belgium; and superphosphate, from Belgium and the Netherlands. As Sweden was in a position to trade with Germany during the war, it was natural that the imports of potash should increase after hostilities commenced. It was just as natural that the imports of phosphate should fall to a low figure, that the imports of sodium nitrate should be cut in half, and that outside supplies of superphosphate and Thomas phosphate should be cut off entirely. Calcium nitrate has been imported from Norway since the war started.

The domestic manufacture of fertilizers cannot meet the home demand, but it has grown to great proportions. With normal supplies of phosphate there is a thriving export business in superphosphate, Norwegian and Swedish pyrites being used for the manufacture of the necessary sulfuric acid. The imports of superphosphate mentioned above form only a small part of the consumption. Cyanamide is a product of the electrochemical industry. Swedish iron ores are rich in apatite and yield a rich Thomas slag. Animal waste and bone meal are important domestic items, and the production of fish guano is in normal times a feature of the herring industry, although it practically disappeared during the war.

There was the same shortage of fertilizers during the war as in other countries, as shown by the production and trade statistics included in this article.

PRODUCTION OF MATCHES

Judging from the latest production figures available, the manufacture of Swedish safety matches was stimulated by the war, as the output was increased from 73,000,000 lbs. in 1913 to 114,000,000 lbs. in 1917. It does not appear from the statistics, however, that all of the increased production went into foreign trade, for the export returns are 61,000,000 lbs. for 1913; 85,000,000 lbs. for 1917; 63,000,000 lbs. for 1918; and 61,000,000 lbs. for 1919. Later production figures would probably show a falling output.

Swedish safety matches need no introduction to the outside world, as they were standard for years before the war. They failed to reach the United States during the war, and the character of the substitutes offered, especially by Japan, is still well remembered. It is also common knowledge that the American product was improved, until it is now generally accepted as quite satisfactory. The efforts of the Swedish manufacturers to regain the lost ground will be watched with interest.

The Swedish industry has unlimited supplies of match wood to draw from, both at home and in Finland, most of the material in the past coming from the latter country. The home supplies are in rather inaccessible parts of the country, but these have been opened up to some extent since communication with Finland became uncertain. Phosphorus is now produced by an electric smelting method that promises to supply the needs of the match industry. Potassium chlorate has been manufactured in Sweden for many years, and the production is not only sufficient for the match industry, but supplies a surplus for export. Potassium chloride, the raw material, is imported from Germany. Machinery for making and packing matches has been developed to a state of extraordinary efficiency.

STATISTICS OF PRODUCTION

A comparison of production statistics for 1913 and 1917 will reveal the proportions of the Swedish chemical industry and the effect of war conditions on output—the stimulating effect of war prices, and the depressing effect of decreased imports of raw materials. The table has been compiled from official figures published by the Swedish Department of Commerce, of the Board of Trade.

Production of Chemicals and Allied Products

	1913 Pounds	1916 Pounds	1917 Pounds
Chemicals, Drugs, Etc.:			
Acids:			
Acetic	1,610,675	977,488	973,004
Nitric	1,188,380	4,205,442	3,051,519
Hydrochloric	5,434,167	2,362,958	3,030,077
Phosphoric	1,222,216	963,949	662,242
Sulfuric	185,040,128	168,127,363	121,750,874
Aluminium compounds (hydrate, sulfate, etc.)	12,730,118	38,744,978	36,426,976
Ammonia, liquid	8,080,382	13,081,175	8,945,455
Ammonium:			
Caustic	1,675,480	2,526,036	2,575,142
Nitrate	1,431,408	1,508,193	1,420,083
Sulfate	3,035,014	2,954,827	2,874,902
Calcium carbide	70,441,652	80,153,528	76,437,825
Carborundum	....	110,231	....
Chloride of lime	1,188,064	3,408,346	3,660,195
Chrome alum	....	....	15,400
Coal tar and products:			
Asphaltic, mastic, and similar preparations	15,738,869	14,884,316	9,649,873
Benzene products	(1)	1,506,432	1,636,057
Coal tar	28,728,900	35,269,646	27,006,529
Other coal-tar products	2,552,953	4,637,747	3,295,429
Copper:			
Scales and oxide	....	192,212	154,227
Sulfate	942,586	2,795,351	2,106,517
Cosmetics and toilet preparations	$801,610	$980,212	$1,223,650
Fertilizers	587,339,974	456,088,200	338,027,823
Animal waste	72,294,571	72,015,148	85,365,501
Bone meal	12,832,516	17,714,720	11,812,889
Fish guano	1,287,543	223,119	31,195
Nitrogen carbide	40,460,315	58,222,143	38,830,208
Superphosphate	406,221,652	270,652,594	165,280,410
Thomas phosphate	40.463,419	29,227,776	26,836,449
Other	13,779,958	8,032,700	9,871,171
Ferrous sulfate	706,030	616,170	322,470
Glauber's salts	12,397,112	9,196,141	11,232,681
Glycerol:			
Raw	321,500	1,284,065	648,322
Purified	1,071,898	1,327,919	369,395
Nitrobenzene	....	263,126	251,214
Perfumes	$176,755	$251,104	$410,508
Phosphorus	....	....	222,005
Potash:			
Caustic	310,356	507,063	282,716
Chlorates and perchlorates	7,955,011	9,289,935	10,929.096
Nitrate	....	400,381	373,862
Yellow prussiate	236,708	....	....

[1] Not given separately.

PRODUCTION OF CHEMICALS AND ALLIED PRODUCTS (*Continued*)

	1913 Pounds	1916 Pounds	1917 Pounds
CHEMICALS, DRUGS, ETC. (*Concluded*):			
Soda:			
Bisulfate	....	5,869,385	5,746,511
Caustic	360,425	1,353,171	1,629,029
Crystals	28,418,289	14,965,911	8,122,724
Tanning materials, vegetable	6,261,127	13,182,737	14,191,426
Water glass	2,956,487	2,741,329	1,943,317
GUMS AND RESINS:			
Dextrin and preparations	796,149	1,642,834	1,177,564
Elastic glue for printing cylinders	....	518,086	299,659
Liquid glue and gum	940,428	1,862,004	2,610,855
Marine glue and gelatin	4,207,682	5,430,924	4,500,367
Rosin	137,789	191,114	726,480
Rosin glue	2,764,407	2,002,397	496,327
WOOD-DISTILLATION PRODUCTS:			
Acetate of lime	....	2,449,395	1,799,532
Acetone	....	60,252	108,778
Creosote	....	54,509	15,609
Formalin	278,658	408,651	676,111
Methanol	1,161,289	1,304,559	989,212
Pitch and pitch oil	397,848	727,126	1,763,559
Rosin, liquid	1,747,853	5,313,857	6,619,383
Tar and tar oil	14,553,776	17,177,663	14,639,054
Turpentine oil	1,387,446	4,267,637	4,535,608
Wood oil	376,488	455,863	430,752
Other (including creosote oil)	....	726,076	1,492,346
	Metric Tons	Metric Tons	Metric Tons
ORES, ETC.:			
Copper	5,458	13,895	13,579
Graphite	250	320	211
Gypsum	....	910	....
Iron	7,479,393	6,988,740	6,220,338
Manganese	4,001	8,894	19,873
Manganese, pulverized	73	154	154
Molybdenum	....	3	137
Nickel	....	3,561	4,991
Silver-lead	3,222	3,707	3,709
Sulfur pyrites and manganese pyrites	34,319[1]	97,848	142,366
Zinc	50,752	60,700	51,312
Zincblende	33,853	48,221	9,727
	Pounds	Pounds	Pounds
PAINTS AND VARNISHES:			
Bone-black	132,277	106,042	192,067
Bronze paint	40,371	38,308	35,949
Butter and cheese coloring	166,109	185,519	43,398
Earth colors	1,766,317	2,390,438	1,990,703
Inks, printing	1,916,152	1,061,591	1,680,826
Lacquer and enamels	....	751,743	428,343
Lampblack	1,613,800	1,480,322	1,053,810
Ocher, red	4,549,739	4,479,887	2,713,618
Oil paints	1,629,593	2,770,132	1,788,833
Putty paint	685,159	711,535	513,754
Varnishes	3,438,424	3,819,392	3,422,306
Other colors	695,889	1,870,876	221,529
Other similar preparations	$24,553	$70,280	$55,172
TOTAL, paints and varnishes	$927,707	$2,128,364	$3,102,177
OILS, FATS, AND WAXES:			
Animal oils	150,338	877,677	274,286
Bone fat	1,805,566	1,729,193	2,391,224
Candles	5,351,743	2,943,901	951,085
Greases	5,824,171	5,997,312	2,304,174
Leather oils and greases	640,560	1,243,857	451,798
Linseed oil	19,294,931	20,815,356	....
Linseed-oil substitute	....	691,903	1,735,302
Machine and axle grease	2,401,006	2,177,852	1,932,199
Oilcake:			
Linseed cake and meal	41,466,995	44,603,263	....
Rapeseed cake	1,118,846	678,406	....
Olein and other fatty acids	1,053,111	2,278,389	2,704,395
Oleomargarine	1,328,223	1,187,182	....
Soap and similar products	63,378,621	73,272,959	42,509,212
Soft soap	44,453,715	55,288,907	20,029,208
Soft-soap substitute	....	....	5,070,358
Toilet soap	6,694,373	5,756,072	5,260,130
Other soap	4,562,510	3,797,586	4,550,253
Washing and soap powder	7,668,023	8,430,394	7,599,263
Stearin	2,488,234	2,246,112	975,614
Stearin wax	89,100	154,573	215,017
Tallow:			
"Premier jus"	613,355	1,557,008	99,722
Compressed	659,072	589,152	24,701
Dyretalg	288,975	633,179	195,330
Turnip and rapeseed oils	697,102	433,702	15,432
Other oils and fats	603,747	3,047,209	2,823,423
	Metric Tons	Metric Tons	Metric Tons
MISCELLANEOUS MANUFACTURES:			
Chalk	19,037	19,022	15,435
	Pounds	Pounds	Pounds
Explosives:			
Dynamite and other explosives containing nitroglycerin	4,676,460	5,240,654	5,532,828
Explosives not containing nitroglycerin	186,458	145,520	371,827
Fireworks	$4,824	$8,950	$9,385
Fuses	260,322	410,677	250,313
Guncotton:			
Compressed	61,132	100,853	56,970
Not compressed	635,917	1,450,463	1,066,400
Nitrated	....	518,086	299,659
Powder:			
Black	724,011	530,079	478,657
Smokeless	541,724	1,302,700	1,066,076
MISCELLANEOUS MANUFACTURES (*Concluded*):			
Gases:			
Acetylene[1]	176,577	322,876	395,082
Carbonic acid	1,999,749	1,956,020	1,919,911
Hydrogen	410	5,952	4,702
Oxygen	393,338	967,243	1,367,880
Other	2,538	24,456	49,622
	Cubic Feet	Cubic Feet	Cubic Feet
Gas works:			
Acetylene gas	1,149,718	164,351	94,818
Coal gas	3,038,032,803	3,641,093,300	3,067,932,707
Water gas	55,949,736	178,699,081	249,589,335
	Pounds	Pounds	Pounds
Glass and manufactures:			
Bottles	66,675,066	68,901,531	44,455,756
Flasks and jars for medicines	6,041,556	7,558,724	9,392,998
Window glass	21,410,928	21,588,255	17,043,580
Other glass manufactures	$1,548,740	$2,645,616	$3,425,974
Insulating material	918,536	1,709,358	1,682,581
Mantles, gas and electric	30,776	75,727	65,222
Matches:			
Safety	72,782,851	117,873,166	114,238,116
Other	16,858,807	8,726,715	1,715,723
Paper and pulp:			
Cardboard	107,124,750	173,281,355	120,243,352
Paper	626,918,053	729,480,953	615,313,118
News print	204,552,662	267,615,805	244,104,797
	Metric Tons	Metric Tons	Metric Tons
Pulp	1,186,577	1,324,458	1,023,661
	Pounds	Pounds	Pounds
Sealing wax	122,544	152,165	151,689
Shoe polishes and finishes	1,550,154	4,980,741	4,919,637
Sugar:			
Beet pulp	891,337,572	949,515,408	998,907,069
Cut sugar	16,163,950	16,391,092	14,723,791
Molasses	44,757,155	60,882,120	57,737,621
Raw sugar	290,924,786	280,762,641	302,904,126
Refined sugar	297,072,770	314,957,660	256,608,238
Sirup	8,094,771	30,379,045	27,634,827

[1] Sulfur pyrites only.

[1] See also item under "Gas works."

STATISTICS OF IMPORTS

Swedish trade statistics are published monthly and annually. The latest are to be found in the monthly returns, but the list of chemicals is a short one and the countries of origin are not shown. However, to give an idea of tendencies during the first year of peace, a table has been compiled from these returns showing

SUMMARY OF IMPORTS OF CHEMICALS AND ALLIED PRODUCTS

	1913 Pounds	1918 Pounds	1919 Pounds
CHEMICALS, DRUGS, ETC.:			
Caustic potash and soda	11,669,137	1,779,064	11,599,705
Chloride of lime	....	2,438,711	11,284,073
Fertilizers:			
Phosphate	243,498,202	80,924,806	152,823,478
Thomas phosphate and slag	42,424,088	.....	....
Glycerol, crude and refined	736,969	87,681	1,255,502
Phosphorus, white and red	....	119,996	84,546
Potash salts	176,925,982	232,385,613	275,361,721
Salt, table	53,615,036	50,690,859	31,581,354
Sodium:			
Carbonate and bicarbonate	40,206,516	5,323,997	31,343,438
Nitrate	74,717,450	14,909,492	51,174,253
Sulfate and bisulfate	70,008,208	80,982,088	29,706,451
Sulfur	84,198,112	....	43,798,438
	Metric Tons	Metric Tons	Metric Tons
Sulfur pyrites	131,875	109,652	71,304
	Pounds	Pounds	Pounds
Tanning extracts, vegetable	19,710,861	690,955	28,582,491
COLORS AND DYES:			
Coal-tar colors	2,149,536	927,907	1,484,882
Varnish	1,342,679	232,184	3,626,763
Zinc white, white sulfide of zinc, and white baryta	11,314,192	1,484,882	5,776,334
GUMS AND RESINS:			
Caoutchouc, all kinds	2,348,785	1,119,375	4,530,237
Resins, including turpentine and other native balsams	15,657,259	408,151	9,777,141
OILS, FATS, AND WAXES:			
Mineral oils:			
Benzine and gasoline	(1)	3,058,029	52,695,553
Illuminating oil, purified	265,316,714	43,275,745	163,114,802
Lubricating oil	(1)	25,568,369	51,248,553
Other	130,675,963	17,301,291	91,463,911
Oilcake	346,703,690	14,160,785	151,308,131
Olein and other fatty acids, n. e. s.	1,852,717	15,265	1,286,770
Oleomargarine	1,265,831	....	4,172,721
Paraffin, raw or refined	7,185,792	2,890,522	5,956,324
Tallow	8,293,123	2,489	8,475,276
Turpentine oil	1,099,661	2,438	827,492
Vegetable fixed oils	61,909,522	1,802,316	91,444,740
Whale oil	3,361,219	131,401	986,459
SUGAR	4,683,073	25,464,605	20,804,546

[1] Not stated separately.

the trade in chemicals and allied products in summary form for the years 1913, 1918, and 1919. With this table and the detailed table for 1913, 1916, and 1917 compiled from the annual returns, it will be possible to study the extent and character of the Swedish market for imported chemicals, and the effect the war has had upon it. The tables are based upon publications issued by the Swedish Department of Commerce, of the Board of Trade.

The following table, showing the import trade in detail and by countries, is based upon the latest annual statistics:

IMPORTS OF CHEMICALS AND ALLIED PRODUCTS

	1913 Pounds	1916 Pounds	1917 Pounds
CHEMICALS, DRUGS, ETC.:			
Acetate of lime	198,171	386	28,259
Acids:			
Boric	264,777	159,233	102,579
Germany	178,969	....	....
United Kingdom	75,978	124,186	100,200
Citric and tartaric	203,185	306,881	47,062
France	34,502	126,060	11,102
Germany	106,005	....	....
Italy	....	49,121	....
United Kingdom	31,676	100,617	....
Formic and lactic	251,605	427,234	24,881
Hydrochloric	3,183,470	1,572,775	87,468
Germany	3,141,622	1,471,299	....
Hydrofluoric acid and fluoride of ammonium	59,417	147,452	13,272
Germany	58,570	147,452	....
Nitric	191,848	6,017,951	5,009,204
Denmark	36,528	6,015,414	5,009,204
Germany	155,320	....	....
Oxalic	169,203	1,308,415	890,429
Germany	158,078	1,308,399	890,429
Phosphoric	8,391	2,945	357
Salicylic	19,141	51,176	130
Sulfuric (including sulfurous anhydride)	2,455,733	1,305	115
Germany	1,540,751	....	....
Netherlands	863,207	....	....
Tungstic	906	2,280	....
Albumin	10,721	26,398	119
Alum	99,358	213,855	530,196
Aluminium:			
Pure and hydrate	626,084	32,163	10,873
Sulfate	4,798,925	502,076	2,783,472
Germany	....	303,530	1,754,833
United Kingdom	2,604,402	....	256,938
United States	....	....	672,218
Ammonium:			
Carbonate	367,369	620,641	333,980
Germany	....	27,355	199,236
United Kingdom	344,596	396,821	55,354
Caustic	161,303	16,193	2,150
Nitrate	137,635	327,162	793,519
Germany	79,269	....	....
Norway	57,836	327,162	793,519
Sal ammoniac	429,315	645,033	2,328
Sulfate	83,352	3,091,191	686,394
United Kingdom	....	3,090,741	686,308
Ammonium, potassium, and sodium phosphate	50,788	125,152	35
Germany	49,306	....	....
United States	....	99,880	....
Arsenic, white	80,136	355,149	80,209
Germany	....	355,149	80,209
Barium protoxide (baryta) and barium peroxide (gray powder)	....	148,834	55
Germany	....	148,834	....
Borax	1,036,219	1,099,707	388,756
Denmark	....	69,875	....
Germany	548,843	1,746	....
United Kingdom	483,542	535,342	186,211
United States	....	471,403	202,545
Bromine, potassium bromide, etc.	24,716	39,225	19,074
Germany	24,341	34,540	19,050
Calcium and barium carbide	5,225	18	8,483
Calcium, barium, and aluminium chloride	653,831	2,351,281	513,904
Germany	322,367	2,189,999	468,696
Carbon disulfide and chloride of sulfur	81,192	41,301	24
Carborundum	86,401	248,132	454,893
Denmark	26,403	....	....
Germany	50,014	....	....
Norway	....	200,288	409,577
Switzerland	....	....	43,755
United States	....	39,392	1,561
Casein	459,137	865,361	22,046
Denmark	....	....	22,046
France	244,826	631,404	....
Germany	113,822	....	....
United Kingdom	....	163,012	....
Celluloid	375,181	301,907	201,758
Chemical preparations, n. e. s.	1,438,890	2,037,095	846,383
Germany	1,068,274	1,858,768	[illegible]
CHEMICALS, DRUGS, ETC. (*Continued*):			
Chloride of lime	16,266,542	8,474,650	4,812,742
Belgium	853,270	....	....
Denmark	51,141	452,583	....
Germany	4,485,293	2,589,613	1,558,679
Norway	....	851,438	255,145
United Kingdom	10,876,837	1,323,069	....
United States	....	3,109,748	2,796,826
Chrome acetate and iron acetate	8,717	2,802	220
Chrome alum	453,039	43,283	44,077
Chromium sulfate	1,627	36,354	33
Coal tar and products:			
Benzene oils	461,773	1,940,127	206,311
Germany	218,403	1,832,669	184,333
Norway	84,471	....	....
United Kingdom	120,803	....	....
United States	....	107,458	....
Carbolic acid, cresol, and creosote oil	8,225,762	4,713,924	113,559[1]
Germany	3,057,200	36,369	....
United Kingdom	5,136,797	4,667,440	....
Carbolineum	306,054	2,425	492
Coal tar	14,723,234	4,852,424	2,439,397
Denmark	7,616,168	....	220,460
Germany	4,487,792	....	....
Norway	1,066,266	1,030,298	589,565
United Kingdom	1,552,953	3,568,540	1,629,371
Naphthalene	216,399	709,226	618,635
Germany	190,341	675,216	605,522
Other coal-tar products	584,995	291,309	55,071
United Kingdom	356,162	138,960	....
United States	....	125,012	....
Copper:			
Oxide	7,211	231	....
Sulfate	145,062	111,622	1,008
Drugs and toilet preparations:			
Hair dye	7,319	7,681	6,475
Perfumery and cosmetics	58,034	63,554	67,833
Salicylic preparations	47,291	99,826	15,009
Germany	44,597	93,909	14,647
Tartar emetic	27,262	5,057	450
Toilet water	42,485	32,926	9,081
Tooth powder and paste	3,287	3,591	2,277
Other drugs	261,772	371,308	126,011
British South Africa	....	3,552	23,874
Denmark	20,456	15,562	11,883
Germany	197,400	196,187	35,207
Netherlands	....	6,515	22,912
Russia, European	....	43,089	....
United Kingdom	18,336	56,431	15,582
United States	....	21,215	....
Fertilizers:			
Calcium nitrate	....	2,280,084	3,159,158
Norway	....	2,280,084	3,159,158
Nitrogen carbide	110	37	....
Phosphate, raw	271,717,082	189,436,304[2]	3,863,782
Australia	37,116,513	....	....
Germany	49,265,777	....	....
Tunis	22,300,836	19,764,695	....
United Kingdom	73,915,963	....	....
United States	76,106,516	131,470,331[2]	....
West Indies	....	14,273,934	3,863,782
Potash salts:			
37 per cent potash	63,110,907	106,170,904	32,354,622
Germany	63,110,691	106,170,904	32,354,622
20 per cent potash	61,799,524	120,812,090	59,352,465
Germany	61,796,878	120,812,090	59,352,465
12 per cent potash	51,725,248	5,516,150	....
Germany	51,607,697	5,516,150	....
Other	1,713	176,370	419
Sodium nitrate	74,718,261	80,159,488	37,848,293
Chile	232,524	70,196,432	....
Germany	72,873,155	....	....
United States	....	....	35,252,615
Superphosphate	7,188,092	3,261	....
Belgium	3,985,223	....	....
Netherlands	2,830,786	....	....
Thomas phosphate and slag	46,670,839	3,406,141	....
Belgium	14,282,845	....	....
Germany	703,715	3,406,141	....
United Kingdom	30,517,817	....	....
Formalin	19,279	48,627	112
Glycerol:			
Crude	43,512	585,632	668,000
Denmark	....	462,990	414,710
Finland	33,658	....	....
Norway	....	122,642	67,547
United States	....	....	185,743
Refined	694,925	39,804	778
Germany	206,026	....	....
Netherlands	357,119	39,804	....
United Kingdom	113,089	....	....
Hydrogen peroxide	153,814	270,992	94,177
Germany	....	268,836	94,177
Insect powder	18,686	44,198	29,943
Iodine, potassium iodide, etc.	11,574	13,400	1,680
Germany	11,570	12,749	....
Iron:			
Oxyhydrate	9,163,781	5,665,433	1,938,712[3]
Germany	7,909,374	1,291,578	....
Netherlands	1,111,130	3,723,481	....
Sulfate	1,660,495	231,302	143,360
Germany	1,004,062	....	....

[1] Not given by countries.

[2] Including 11,460,784 lbs. of "apatit."

[3] Not given by countries in 1917.

IMPORTS OF CHEMICALS AND ALLIED PRODUCTS (*Continued*)

	1913 Pounds	1916 Pounds	1917 Pounds
CHEMICALS, DRUGS, ETC. (*Continued*):			
Lead:			
Nitrate	1,678	430	137
Oxide and peroxide	719,917	1,492,957	90,407
Germany	438,636	496,232	....
United Kingdom	164,659	881,999	....
Sugar of lead and lead vinegar	145,454	66,983	27,928
Magnesia, calcined or carbonate	75,111	379,980	336,807
Magnesium:			
Chloride	1,759,456	7,215,702	1,528,163
Germany	1,659,163	7,180,621	1,527,259
Sulfate	1,612,458	3,870,492	968,610
Germany	1,619,147	3,825,770	968,610
Nickel oxide and sulfate	71,231[1]	108,866	89,852
Nitrate of silver	1,215	2,449	432
Nitrobenzene	142,832	2,216	....
Phosphorus	203,899	228,677	46,709
United Kingdom	184,218	222,285	37,018
Phosphorus sesquisulfide and hydride	70,140	114,861	....
United Kingdom	69,898	114,861	....
Potash	3,124,528	6,020,191	3,920,782
Germany	2,761,228	5,910,621	3,880,752
Potash, yellow prussiate of	25,142	253,256	363,723
Germany	....	250,189	363,692
Potassium:			
Chloride	4,586,802	9,768,016	4,067,623
Germany	4,584,574	9,682,029	4,067,616
Nitrate	661,836	7,687	21,881
Germany	641,378	....	....
Sulfate	125,465	308,347	37,101
Germany	125,443	308,347	....
Potassium and sodium:			
Arsenite	77	1,437	3,748
Caustic:			
Solid	4,282,697	6,997,643	1,466,250
Germany	573,718	6,138,301	1,256,591
Netherlands	104,845	186,870	....
United Kingdom	3,469,663	116,468	....
United States	....	506,812	176,268
Liquid	7,257,068	12,112,326	1,705,421
Germany	7,173,445	12,077,640	1,623,266
Chlorate	558,740[2]	399	7
Chromate	308,233	220,537	260,650
Germany	68,323	1,373	....
United Kingdom	219,012	20,849	12,070
United States	....	173,250	248,580
Cyanide	16,793	28,892	31,976
Potassium, sodium and calcium sulfide	1,273,679	3,164,497	610,244
Germany	654,969	3,032,452	565,907
United Kingdom	523,058	....	....
Rennet	256,268	162,494	61,291
Saccharin	....	1,385	220
Salt, common	54,954,351	61,889,071	47,797,440
Germany	39,338,635	48,057,912	47,355,920
United Kingdom	12,040,373	11,515,241	....
Salts:			
Formaldehydesulfoxylic acid	17,205	9,572	5,234
Gold, platinum, and radium salts	95	161	49
Stannate, stannic chloride and putty powder	125,624	65,733	38,036
Soda	40,726,788	32,997,872	8,420,134
Germany	32,949,191	17,424,528	5,491,199
United Kingdom	4,682,840	4,060,383	433,405
United States	....	10,403,531	2,386,420
Sodium:			
Acetate	68,881	584	445
Sulfate and bisulfate	69,975,599	121,152,066	102,081,969
Belgium	2,250,368	....	....
Germany	11,481,468	78,800,963	98,525,118
Netherlands	....	18,766,530	3,306,250
United Kingdom	54,026,473	22,233,088	....
Sulfite	649,885	2,898,465	682,600
Germany	434,364	2,815,946	646,695
Sulfur	87,557,545	59,268,010	32,195,890
Germany	6,476,439	....	....
Italy	49,181,777	43,863,181	....
United Kingdom	23,340,804	8,328,587	11,199
United States	8,536,780	7,076,238	32,184,682
Tanning materials:			
Catechu	452,728	184,066	4,220
Germany	439,456	....	....
United Kingdom	....	178,705	....
Oak bark	364,094	....	50,300
Quebracho	10,777,774	9,327,041	969,328
Argentina	696,169	6,992,621	611,377
Belgium	664,486	....	....
France	709,469	....	....
Germany	6,315,498	58,360	....
United Kingdom	2,233,377	50,600	....
United States	....	1,333,459	157,951
Tannic acid	189,443	33,503	2,046
Other	8,407,557	1,428,506	52,902[3]
France	3,387,095	....	....
Germany	2,740,108	303,800	....
United Kingdom	620,491	496,233	....
United States	....	476,632	....
CHEMICALS, DRUGS, ETC. (*Concluded*):			
Tartar	56,732	270,999	68,965
Denmark	....	22,399	22,046
France	36,332	49,926	....
Italy	....	66,529	46,297
Spain	....	93,053	....
United Kingdom	....	23,089	622
United States	....	10,935	....
Thorium nitrate	4,799	12,154	13,726
Water glass	1,653,160	2,716,593	1,498,440
Germany	1,120,826	2,239,352	1,367,701
Norway	....	186,105	120,798
United Kingdom	....	236,078	....
Zinc sulfate and chloride	314,077	503,346	139,614
Germany	....	494,958	139,614
COLORS AND DYES:			
Bone-black	243,725	168,839	27,212
Germany	....	144,398	....
Bronze and color leaf	5,454	8,087	6,975
Germany	4,394	7,635	6,766
Bronze powder	22,661	14,339	26,451
Butter and cheese coloring	21,118	12,489	4,561
Chalk:			
Ground, washed, or precipitated	3,321,223	1,372,802	1,381,850
Denmark	2,477,518	....	....
Germany	706,995	588,335	308,595
For schools, and French chalk	88,654	97,082	82,309
Colors for typographic, lithographic, and plate printing	58,220	105,888	49,348
Germany	47,633	64,833	34,469
Colors prepared with oil:			
For ships' bottoms	415,840	335,464	83,934
Germany	85,608	45,051	....
Norway	....	....	20,968
United Kingdom	282,053	266,668	....
United States	....	....	35,783
Other	135,221	177,763	88,390
Dyes:			
Alizarin dyes	136,596	78,143	54,494
Germany	128,940	77,978	54,494
Aniline and other tar dyes	2,049,538	1,768,552	1,835,070
Denmark	20,741	18,607	....
Germany	1,873,519	1,728,450	....
Netherlands	50,115	....	....
Switzerland	87,096	18,062	....
Cochineal	1,312	1,360	99
Dyestuffs:			
Aniline (aniline oil)	52,523	30,190	22,641
Germany	49,886	18,735	11,442
United States	....	11,455	11,199
Dyewoods	551,170	198,859	2,303,673
Whole or in pieces	....	2,183	2,255,306
Ground	....	....	....
Brazil wood	171,397	23,677	1,102
Other	379,773	65,164	2,152
Germany	357,646	64,998	....
Extracts	232,940	65,821	45,029
Other vegetable dyestuffs	13,397	42,015	84
Indigo	191,399	84,994	68,091
Natural	1,345	359	....
Synthetic	115,376	40,917	42,935
Germany	110,104	38,036	42,935
Other indigo coloring matters	74,679	43,717	25,157
Germany	74,679	39,707	....
Earth colors	3,822,082	4,889,477	2,728,786
France	953,587	1,307,121	....
Germany	2,536,275	3,440,638	2,560,612
Ink, ink powder, and India ink	43,740	48,810	32,624
Germany	24,928	33,010	....
Ink, printer's	187,702	119,562	57,626
Denmark	25,095	11,790	26,131
Germany	155,982	100,043	28,424
Lampblack	293,046	705,763	308,340
Germany	212,418	594,129	299,662
Mineral colors	20,442,170	39,169,627	13,362,960
Cobalt oxide	22,811	10,538	14,423
Germany	14,156	....	9,367
United Kingdom	8,060	6,367	....
Red ocher	1,432,068	1,341,815	477,254
Germany	950,662	827,364	349,719
United Kingdom	463,473	514,451	127,535
Red lead	2,589,373	4,629,058	276,118
Germany	949,474	2,107,601	....
Netherlands	300,128	148,812	....
United Kingdom	1,234,256	2,370,022	....
United States	....	2,646	144,169
White lead	1,341,310	2,172,587	4,965
Germany	809,008	1,089,765	....
Netherlands	390,851	485,017	....
United Kingdom	126,332	350,755	....
United States	....	220,462	....
White sulfide of zinc and white baryta	2,681,499	8,642,199	2,544,368
Belgium	266,462	....	....
Denmark	....	....	151,171
Germany	1,460,304	8,093,907	2,393,197
Netherlands	811,369	448,524	....
United Kingdom	104,087	....	....
Zinc white	8,707,802	16,185,980	7,303,080
Belgium	206,540	51,809	....
Denmark	69,931	337,969	....
Germany	5,810,705	14,387,472	5,915,839
Netherlands	2,424,277	1,199,050	1,364,452
United Kingdom	120,505	....	....
United States	....	204,082	....

[1] All sulfate.
[2] All potassium chlorate.
[3] Not given by countries.

IMPORTS OF CHEMICALS AND ALLIED PRODUCTS (*Continued*)

	1913 Pounds	1916 Pounds	1917 Pounds
COLORS AND DYES (*Concluded*):			
Mineral Colors (*Concluded*):			
Other	3,667,283	6,187,418	2,742,775
Belgium	326,987	....	....
Germany	2,597,210	5,834,909	2,636,481
Netherlands	368,348	170,519	....
United Kingdom	322,713	122,509	63,220
Pastilles and black chalk	48,744	88,905	52,223
Germany	39,427	80,221	45,185
Tar colors, with addition of solvents	109,730	136,956	60,305
Germany	56,581	80,825	53,345
Varnish:			
Spirit	30,556	33,843	3,082
Oil	235,709	113,230	247,546
Finland	....	....	165,089
Germany	98,896	....	....
Netherlands	109,386	....	....
United Kingdom	....	79,725	15,964
United States	....	....	51,008
Other	1,090,402	1,012,692	430,137
Germany	344,965	96,334	....
Netherlands	212,614	49,557	....
United Kingdom	249,484	293,152	29,573
United States	257,574	556,002	370,975
OILS, FATS, AND WAXES:			
Acetone and acetone oil	141,593	182,944	29,077
Germany	140,246	32,635	....
United States	....	144,679	29,046
Animal fat	471,637	1,112,809	405,675
Denmark	....	....	396,718
Norway	435,711	....	....
United Kingdom	....	1,082,893	....
Animal oils	3,641,847	511,518	675,340
Denmark	1,125,234	108,398	527,049
Norway	1,623,002	288,016	77,712
Bitter-almond oil	15,016	4,015	1,462
Ceresin	146,736	221,340	1,213
Germany	135,373	92,836	....
United Kingdom	....	55,917	....
United States	....	72,364	....
Collodion	7,321	2,112	3,779
Degras (tanners' fat)	294,885	220,420	....
Germany	280,086	47,577	....
Norway	....	48,197	....
United Kingdom	....	74,630	....
United States	....	50,016	....
Disinfectants containing soap	49,066	5,975	4,786
Greases:			
Machine and wagon grease	1,832,558	1,254,400	223,630
Belgium	426,976	....	....
Denmark	....	152,349	....
Germany	890,438	....	....
United Kingdom	271,549	84,809	....
United States	....	1,014,896	127,216
Other	894,433	612,537	379,689
Belgium	219,433	....	....
Denmark	....	203,886	....
Germany	419,452	....	....
United Kingdom	176,536	287,925	135,717
United States	....	118,594	222,332
Lanolin	188,780	103,043	33,420
Germany	160,252	....	....
United Kingdom	....	95,322	29,107
Lubricating oils (mixed fatty and mineral oils)	2,462,878	1,567,016	1,229,413
Finland	....	....	402,556
Germany	1,005,474	....	....
United Kingdom	866,862	95,164	....
United States	246,256	1,397,128	751,506
Mineral oils:			
Crude	37,167,287	23,581,010	8,113,219
Austria	27,867,729	....	204,190
United Kingdom	502,362	2,244,530	....
United States	3,610,745	21,323,497	7,894,371
Refined:			
Benzine and gasoline	33,981,235	32,334,174	7,447,485
Netherlands	14,403,386	....	....
United Kingdom	5,110,596	1,985,998	....
United States	12,782,026	30,282,037	7,419,039
Illuminating	265,601,092	239,450,380	82,346,019
Denmark	38,168,575	17,046,600	....
United States	207,951,263	222,262,172	82,245,301
Lubricating	49,323,981	50,978,809	15,227,069
Denmark	1,128,114	5,962,297	635,311
Germany	10,932,215	....	....
Russia, European	25,423,939	....	2,227,839
United States	10,332,103	44,904,327	11,093,007
Other	10,601,092	12,767,967	83,288
Austria	1,643,759	....	....
Denmark	1,873,659	....	....
Netherlands	2,742,295	....	....
United Kingdom	3,475,058	253,802	....
United States	....	12,483,883	....
Olein	1,831,191	3,213,998	1,113,991
Belgium	945,612	....	....
Netherlands	436,401	238,088	....
United Kingdom	....	2,333,838	572,883
United States	....	577,934	362,020
Oleomargarine	1,289,969	3,086,802	1,111
France	599,733	519,653	....
Norway	66,310	2,473,178	....
Oilcake:			
Cottonseed	20,911,601	92,112,205	66,413,156
Argentina	....	2,735,909	....
Denmark	3,178,835	....	....
Germany	3,989,041	....	....
Russia, European	2,624,570	....	....
United Kingdom	1,573,899	....	....
United States	9,434,857	88,811,775	66,413,156
OILS, FATS, AND WAXES (*Continued*):			
Oilcake (*Concluded*):			
Hempseed	959,687	....	....
Germany	649,235	....	....
Russia, European	277,244	....	....
Linseed	9,609,992	....	....
Denmark	876,340	....	....
Germany	1,314,702	....	....
Russia, European	7,373,756	....	....
Peanut	191,552,661	46,711,168	....
France	183,175,174	41,295,053	....
Soy bean	17,499,579	....	....
Denmark	7,291,809	....	....
Germany	5,674,385	....	....
United Kingdom	4,533,385	....	....
Sunflower seed	81,659,242	2,848,367	662,041
Denmark	5,395,066	....	....
Germany	5,962,998	....	....
Russia, European	69,709,337	1,529,772	662,041
Turnip and rapeseed	27,985,739	5,189,736	5,044,081
Argentina	314,226	5,189,736	4,272,471
France	3,839,725	....	....
Germany	20,068,835	....	....
Netherlands	1,485,938	....	....
United Kingdom	992,070	....	....
United States	....	....	771,610
Other	927,786	....	....
Denmark	503,718	....	....
Germany	288,926	....	....
Ozokerite	91,685	84,247	26,515
Paraffin:			
Crude	1,884,219	1,505,138	237,310
Denmark	232,171	....	....
United Kingdom	1,252,579	397,075	1,107
United States	288,752	1,108,043	236,203
Refined	4,853,938	3,485,131	1,433,034
Austria	548,945	....	....
Germany	1,569,695	186,540	....
United Kingdom	632,908	466,648	....
United States	1,996,744	2,814,811	1,414,884
Resinous oils	527,589	153,758	....
Belgium	121,220	....	....
Germany	199,653	....	....
United Kingdom	198,965	113,903	....
Stearin (stearic acid)	374,379	232,912	71,861
Belgium	89,754	....	....
Netherlands	255,019	40,829	....
United Kingdom	....	153,561	....
United States	....	36,499	71,105
Tallow:			
"Premier jus"	3,589,007	4,226,653	....
Argentina	19,299	950,818	....
France	904,946	....	....
Germany	593,838	....	....
Netherlands	862,492	....	....
Norway	45,002	1,233,619	....
United Kingdom	318,902	16,426	....
United States	649,861	2,025,789	....
Compressed	943,487	1,000,179	....
Argentina	....	224,636	....
China	112,803	....	....
France	557,303	132,276	....
United Kingdom	124,066	402,185	....
United States	91,564	228,776	....
Other	3,826,246	3,388,391	88,479
Denmark	641,805	....	22,165
France	364,180	165,998	....
Germany	231,005	....	....
Norway	403,310	74,064	....
United Kingdom	1,485,739	528,489	....
United States	388,263	2,597,795	66,279
Textile-dressing preparations containing soap	157,109	97,097	283,247
Turpentine oil	1,136,800	715,280	28,479[1]
Belgium	224,170	....	....
Finland	....	110,239	....
France	590,222	109,320	....
Germany	281,106	....	....
United Kingdom	....	334,491	....
United States	....	155,283	....
Vaseline	778,133	183,672	174,688
Vegetable oils:			
Fixed:			
Coconut and palm kernel:			
Purified	18,731,058	6,718,856	636,457
Belgium	1,332,723	....	....
Denmark	862,060	381	....
Germany	11,602,841	....	....
Netherlands	208,952	2,507,426	....
Norway	463,691	2,315,379	....
Spain	....	....	259,642
United Kingdom	379,244	380,834	270,994
United States	....	62,238	....
Other	9,066,653	2,196,838	46,749
France	4,715,463	917,559	....
Germany	2,411,530	....	....
United Kingdom	1,025,382	738,640	46,749
Cottonseed	5,267,964	11,553,764	....
Germany	324,061	....	....
Netherlands	1,983,205	....	....
Norway	....	1,568,178	....
United Kingdom	799,392	73,841	....
United States	1,955,582	9,911,745	....
Hemp and castor	1,910,621	498,751	20,434
Denmark	708,472	....	....
Germany	277,766	....	....
Netherlands	....	235,700	....
United Kingdom	634,162	238,842	....

[1] Not given by countries.

IMPORTS OF CHEMICALS AND ALLIED PRODUCTS (*Continued*)

	1913 Pounds	1916 Pounds	1917 Pounds
OILS, FATS, AND WAXES (*Concluded*):			
Vegetable oils (*Concluded*):			
Linseed:			
Raw	762,196	560,222	79,048[1]
Belgium	55,294	....	....
Germany	76,967	....	....
Netherlands	625,432	....	....
United Kingdom	....	363,400	....
United States	....	194,089	....
Boiled	30,492	14,367	549,289
Finland	....	....	526,368
Maize	4,950,689	986,475	33,356
United Kingdom	4,026,038	181,333	33,356
United States	427,942	805,142	....
Olive	731,182	1,206,712	88,781
Palm	1,922,030	1,327,189	109,392
Germany	247,603	....	....
United Kingdom	1,642,808	1,326,484	109,392
Peanut	3,123,601	1,390,551	....
France	578,633	1,314,166	....
Germany	1,877,675	....	....
Sesame	4,445,876	310,119	10,079[1]
Germany	3,459,765	....	....
Netherlands	469,946	297,121	....
Soy bean	9,326,366	14,993,004	86,127
China	1,028,660	1,927,142	....
Denmark	2,881,397	1,260,612	....
Germany	1,237,239	....	....
Japan	2,053,907	11,655,868	....
United Kingdom	1,348,849	18,739	86,127
United States	....	130,642	....
Turnip and rapeseed	206,988	411,213	66,451
United Kingdom	167,724	237,411	55,931
United States	....	173,568	....
Other	1,364,522	794,478	40,386
China	392,703	105,380	....
Germany	376,537	....	....
United Kingdom	336,069	353,221	....
United States	57,827	93,133	....
Volatile	54,335	89,368	70,353
France	3,732	10,613	5,168
Germany	41,654	45,847	39,793
Italy	4,107	8,459	4,610
United Kingdom	1,484	13,750	6,334
United States	....	1,021	7,930
Wax:			
Beeswax	35,137	29,531	4,012
Sealing wax	22,901	12,385	1,664
Vegetable (carnauba, palm, etc.)	58,190	221,368	64
France	....	33,283	....
Germany	55,115	....	....
United Kingdom	....	81,579	....
United States	....	47,271	....
Wax manufactures	1,651	1,512	1,085
Wood oil	1,601	1,607	....
TARS, GUMS, RESINS, ETC.:			
Camphor	44,361	34,694	8,913
Caoutchouc, gutta-percha, etc.:			
Dissolved or paste	296,971	38,728	229
Soft rubber, artificial	43,327	55,230	22,458
Unmanufactured	2,069,628	2,586,159	1,033,536
Denmark	398,305	590,220	1,026,400
Germany	234,931	132	....
United Kingdom	907,021	1,774,807	....
Waste rubber	281,832	291,380	34,334
Coal tar prepared for covering roofs	185,513	48,309	2,418
Dextrin	409,718	50,075	27,057
Gelatin:			
Manufactures	1,570	2,747	417
Sheets	9,251	23,455	15,807
Glue:			
Elastic glue for printing cylinders	44,273	27,571	14,526
Liquid glue and gum	25,194	29,196	41,219
Marine glue, etc., not liquid:			
Agar-agar	17,183	42,075	3,785
Gelatin glue	47,588	57,112	17,077
Isinglass	218	13,774	575
Other	231,779	303,665	277,987
Germany	37,155	91,062	....
Netherlands	....	....	169,610
United Kingdom	110,540	144,266	51,571
Vegetable	1,856	3,821	....
Gum, natural	564,941	708,184	45,142
France	23,916	616,900	32,666
Germany	432,450	....	....
United Kingdom	64,673	73,310	....
Pitch of coal or wood tar	8,720,615	7,331,933	307,447[1]
Germany	389,401	3,014,727	....
United Kingdom	7,887,305	3,865,100	....
Resin soap and tanners' glue	198,291	57,198	....
Belgium	54,537	....	....
United States	124,626	49,017	....
Resins:			
Colophony	6,356,911	5,214,438	113,406
France	302,750	1,286,311	....
Germany	5,137,382	33,237	....
Norway	120,505	957,276	111,854
United States	549,956	2,863,050	....
Copal	303,722	1,080,962	....
Germany	147,884	289	....
Norway	....	521,371	....
United States	....	424,070	....

[1] Not given by countries.

IMPORTS OF CHEMICALS AND ALLIED PRODUCTS (*Concluded*)

	1913 Pounds	1916 Pounds	1917 Pounds
TARS, GUMS, RESINS, ETC. (*Concluded*):			
Resins (*Concluded*):			
Shellac	369,076	355,471	87,504
Finland	....	....	49,132
France	....	109,706	....
Germany	219,777	....	....
United Kingdom	139,903	226,734	31,707
Other	8,574,570	13,162,984	13,111[1]
France	318,674	964,946	....
Germany	7,964,465	49,833	....
Norway	....	1,778,892	....
United Kingdom	....	2,727,338	....
United States	....	7,336,478	....
Tar oils	1,367,344	68,142	47,924
Germany	1,270,784	....	....
Terpineol, safrol, and menthol	23,345	60,091	33,027
Germany	20,695	5,256	4,947
United Kingdom	....	52,589	23,029
United States	....	....	3,697
Turpentine	51,074	15,628	2,560
Wood tar and tar water	740,530	2,825,508	1,420[1]
Finland	291,142	2,795,323	....
Russia, European	320,520	....	....
MISCELLANEOUS MATERIALS AND MANUFACTURES:			
Asphalt	15,011,196	13,957,137	9,452,148
Germany	13,185,139	9,281,708	7,820,340
United Kingdom	660,957	3,320,335	899,803
United States	....	590,445	372,600
Candles	51,006	152,305	25,562
Explosives	567,744	342,756	180,279
Gases	76,278	51,564	4,506
Carbonic acid	4,742	112	....
Oxygen and hydrogen	5,258	(2)	439
Other	66,278	51,452	4,067
Glass	8,378,995	13,254,494	11,323,304
Gypsum, precipitated	152,897	93,714	916,693
Germany	....	....	916,693
Insulating material	368,702	671,693	578,802
Germany	329,799	621,805	575,685
Mica, unmanufactured	78,903	237,733	81,511
	Metric Tons	Metric Tons	Metric Tons
Ores, etc.:			
Copper	10	773	555
Graphite	576	719	668
Germany	413	483	629
United Kingdom	....	111	28
Iron	2,909	34	....
Magnesite and witherite	962	992	948
Manganese	854	276	....
Germany	791	5	....
United States	....	246	....
Sulfur pyrites	141,005	128,005	103,894
Norway	86,416	124,312	102,443
Spain	25,102	3,661	1,451
Zinc	12,628	12	....
Other	181	6,309	2,136
	Pounds	Pounds	Pounds
Paper and pulp:			
Cardboard	8,374,480	2,884,712	1,320,311
Paper	5,461,526	8,387,967	4,863,647
News print	....	43,697	....
	Metric Tons	Metric Tons	Metric Tons
Pulp	4,947	4,128	1,552
	Pounds	Pounds	Pounds
Polishes for leather goods	257,585	84,101	25,390
Putty	127,554	74,961	23,823
Soap:			
Perfumed	35,126	104,405	111,890
Soft	56,277	26,235	7,035
Other	735,501	1,972,890	572,246
Finland	....	....	213,033
France	104,829	380,503	....
Germany	80,926	28,651	....
United Kingdom	520,292	1,285,447	312,046
United States	....	256,618	....
Sugar	4,751,410	582,812	15,666,948
Vinegar and acetic acid	136,621	98,819	80,558
Washing, cleansing, and polishing substances	480,548	263,046	202,810
Germany	248,108	41,219	....
United Kingdom	171,840	195,065	147,583

[1] Not given by countries.
[2] Not stated separately.

STATISTICS OF EXPORTS

The export returns have been compiled from the same sources as the import figures—that is, a summary table has been based upon late monthly statistics and covers the years 1913, 1918, and 1919, while the detailed table has been compiled from the annual publications for 1913, 1916, and 1917. These publications are issued by the Swedish Department of Commerce, of the Board of Trade.

SUMMARY OF EXPORTS OF CHEMICALS AND ALLIED PRODUCTS

	1913 Pounds	1918 Pounds	1919 Pounds
Chalk, ground, washed, or precipitated	19,683,467	11,640,689	7,618,037
Chemicals, drugs, etc.:			
Calcium and barium carbide	....	8,934,408	6,330,635
Copper sulfate	551,796	662,156	464,434
Fertilizers:			
Cyanamide	....	848,991	1,230
Superphosphate	79,447,146	....	24,600,029
Potassium and sodium chlorate	3,281,675[1]	1,428,717	114,710
Methanol, raw and refined	856,461	14,716	585,057
Glass flasks and bottles	28,526,157	8,473,526	12,643,571
Matches:			
Safety	61,208,799	62,845,247	60,509,517
Other	15,491,521	27,948	2,149,763
Oils, fats, and waxes:			
Rubber waste	1,400,148	894,433	61,925
Tallow	1,160,261	....	17,674
Turpentine oil	488,522	69,169	734,324
Ores:	Metric Tons	Metric Tons	Metric Tons
Iron	6,439,950	4,485,500	2,418,989
Zinc	47,191	16,210	55,138
Paper and pulp:			
Pulp	1,006,456	714,306	902,497
	Pounds	Pounds	Pounds
Cardboard	56,690,440	45,081,574	45,112,423
Paper	409,736,822	283,996,245	307,431,434
News print	135,694,285	94,190,834	145,650,850
Tars, gums, and resins:			
Wood tar and tar water	17,066,399	9,948,518	18,138,466

[1] Potassium chlorate only.

Following is the detailed table of exports compiled from the latest official annual publications. Of special interest are the figures showing the extent to which Germany depended upon Sweden for certain essentials during the war.

EXPORTS OF CHEMICALS AND ALLIED PRODUCTS

	1913 Pounds	1916 Pounds	1917 Pounds
CHEMICALS, DRUGS, ETC.:			
Acetate of lime	1,775,274	605,284	95,453
Denmark	591,135	119,117	....
Germany	....	66,929	....
Norway	....	....	95,453
United Kingdom	995,659	419,238	....
Acids:			
Boric	485	18,289	1,726
Citric and tartaric	2,665	138,493	....
Russia, European	....	121,930	....
Hydrochloric	1,819	860,696	2,618,168
Denmark	....	522,839	1,976,278
Norway	....	359,903	444,778
Hydrofluoric acid and fluoride of ammonium	....	20,152	1,250
Nitric	....	200,738	63,263[1]
Austria	....	57,655	....
Finland	....	80,298	....
Oxalic	635	847,111	410,635
Finland	....	219,133	....
France	....	103,621	201,465
Russia, European	....	410,611	....
United States	....	33,067	98,685
Phosphoric	145,098	218,061	122,086
Denmark	....	68,303	....
Norway	107,357	91,489	89,401
Russia, European	....	44,443	....
Sulfuric:			
Fuming	1,452,459	259,660	398,411
Norway	1,452,459	251,075	397,088
Other	140,323[1]	3,087,392	3,530,704
Denmark	....	637,050	2,050,327
Norway	....	2,384,354	1,470,111
Albumin	....	18,078	....
Germany	....	15,873	....
Alum	13,534[1]	265,354	298,053
Denmark	....	190,546	200,127
Aluminium sulfate	1,398,080	18,377,078	19,978,758
Denmark	1,351,640	2,722,240	1,390,867
Finland	....	7,946,176	14,604,959
Norway	....	6,095,410	2,968,527
Russia	....	1,613,251	1,014,405
Ammonia:			
Caustic	14,286[1]	82,838	194,735
Norway	....	51,691	123,676
Sal ammoniac	2,013	138,755	33,208
Sulfate	560,848	1,609	....
Germany	560,630	....	....
Ammonium, potassium and sodium phosphate	1,433	88,638	....
Germany	....	88,638	....
Arsenic, white	....	7,308	....
Barium protoxide (baryta) and barium peroxide (gray powder)	....	123,647	....
Russia, European	....	123,647	....
Borax	8,563[1]	175,742	....
Austria	....	47,070	....
Germany	....	118,870	....
CHEMICALS, DRUGS, ETC. (*Continued*):			
Calcium and barium carbide	29,954,634	32,430,250	28,505,776
Belgium	2,430,020	....	286,601
British South Africa	487,217	....	....
Chile	....	467,380	....
Denmark	709,286	1,899,814	1,358,047
Finland	....	718,810	....
Germany	4,495,270	5,509,736	14,262,902
Netherlands	1,660,081	10,439,828	7,175,973
Norway	4,244,098	....	....
Portugal	1,321,437	....	....
Russia, European	....	6,349,998	1,440,486
United Kingdom	14,131,473	6,837,457	3,548,138
Calcium, barium and aluminium chloride	....	777,366	264,290[1]
Finland	....	274,151	....
Russia, European	....	450,442	....
Carbon disulfide and chloride of sulfur	....	44,313	....
Russia, European	....	44,092	....
Carborundum	....	291,252	35,770
Finland	....	202,572	....
Germany	....	71,731	....
Russia, European	....	....	23,589
Casein	329,835	332,542	114,390
Denmark	139,203	....	....
Germany	143,784	295,262	114,390
Chemical products not specifically mentioned	802,847	3,012,335	4,344,469
Germany	127,677	260,136	1,077,853
United Kingdom	505,378	2,384,579	3,160,989
United States	....	107,099	....
Chloride of lime	180,987	....	85,980
Copper:			
Oxide	159,889	469,988	626,990
Germany	159,889	398,684	602,508
Sulfate	551,796	1,543,308	1,388,237
Austria	....	418,654	1,167,997
Germany	356,358	....	....
Hungary	....	1,124,655	....
Russia, European	184,194	....	....
Turkey, European	....	....	220,242
Drugs and toilet preparations:			
Drugs	14,842	21,702	30,075
Finland	....	2,233	7,681
Germany	6,715	....	....
Russia, European	....	12,286	17,344
Hair dye	3,349	10,946	3,975
Perfumery and cosmetics	9,185	23,532	11,115
Toilet water	28,073	39,271	36,947
Tooth powder and paste	14,352	15,604	7,019
Fertilizers:			
Cyanamide	37,323,444	42,600,004	6,428,455
Germany	33,399,029	42,554,589	6,428,455
Potash salts	42,770	....	....
Sodium nitrate	2,315	....	5,500
Superphosphate	79,447,166	365,967	670,397
Denmark	39,280,306	365,967	670,397
Finland	5,724,614	....	....
Russia, European	34,429,448	....	....
Thomas phosphate and slag	4,070,904	....	....
Finland	1,269,863	....	....
Russia, European	2,777,824	....	....
Formalin solution	145,704	277,733	467,977
Denmark	84,665	6,537	65,016
Finland	....	90,345	32,297
Germany	....	89,904	275,875
Japan	46,297	....	....
Netherlands	....	22,602	57,470
Glycerol:			
Crude	398,369	5,291	88,185
Germany	393,559	....	88,185
Refined	7,476[1]	269,669	96,903
Denmark	....	44,169	39,683
Norway	....	114,059	37,465
United Kingdom	....	111,440	....
Hydrogen peroxide	397	142,902	61,619
Russia, European	....	138,273	60,075
Iron oxyhydrate	2,579,733	44,092	1,130,475
Iron sulfate	16,867	28,563	992
Lead oxide and peroxide	117,375	885,301	9,724[1]
Germany	99,022	321,466	....
Russia, European	....	556,937	....
Magnesia, calcined or carbonate	....	146,789	130,567
Russia, European	....	123,200	94,158
Magnesium:			
Chloride	84	4,031,918	420,732
Finland	....	955,419	....
Norway	....	....	22,046
Russia, European	....	3,050,869	398,686
Sulfate	1,102	171,538	168,542
Methanol:			
Crude	798,645	564,975	286,064
Germany	675,132	510,039	260,886
Refined	86,328	76,702	91,736
Nitrobenzene	....	78,501	48,051
Denmark	....	20,692	24,777
Norway	....	57,809	23,274
Phosphorus	1,984	6,453	....
Potash	....	306,849	18,254
Norway	....	89,822	....
United Kingdom	....	157,682	....
United States	....	55,080	....

[1] Not given by countries.

Exports of Chemicals and Allied Products (*Continued*)

	1913 Pounds	1916 Pounds	1917 Pounds
Chemicals, Drugs, Etc. (*Concluded*):			
Potash, yellow prussiate of	224,924	196,952	57,465
Russia, European	....	155,702	53,563
United States	112,531	....	....
Potassium chromate	5,172	8,461	....
Potassium and sodium:			
Hydroxide	540,943	900,024	210,004
Solid	539,305	733,971	143,665
Finland	....	106,154	....
Germany	145,801	....	....
Norway	....	171,868	....
Russia	....	89,154	....
United Kingdom	102,252	112,468	....
United States	....	163,350	56,912
Liquid	1,638	166,053	66,339
Chlorate	3,137,384[1]	1,492,400	2,494,492
Denmark	....	417,803	336,396
Germany	708,499	193,125	1,673,308
Japan	745,743	....	....
Norway	560,026	257,585	....
Russia, European	193,187	377,306	125,884
United Kingdom	760,972	141,112	6,614
Cyanide	4	4,566	7,987
Sulfide	1,369	438,482	103,314
Finland	....	130,916	....
Russia, European	....	282,416	....
Rennet	142,790	98,964	73,810
Australia	89,419	58,312	53,290
Salt, table	15,247	3,724,193	....
Finland	....	3,692,429	....
Soda	3,333	116,760	....
Norway	....	47,375	....
Sodium:			
Chlorate	871,686	....	....
Germany	209,439	....	....
Russia, European	496,040	....	....
Sulfate and bisulfate	1,143,548	17,116,918	101,749[2]
Finland	....	17,022,248	....
Germany	796,081	....	....
Sulfite	117	294,257	304,241
Denmark	....	....	25,128
Finland	....	73,036	....
Norway	....	....	219,192
Russia, European	....	183,407	....
Stannous chloride, stannic chloride, and putty powder	19,676	60,463	....
Sugar of lead and lead vinegar	29,537	10,064	....
Sulfur	525,947	....	2,205[2]
Norway	503,780	....	....
Tartar	2,608	168,019	51,297
Germany	....	166,295	150,706
Water glass	....	232,127	193,251[2]
Russia, European	....	118,449	....
Zinc sulfate and zinc chloride	....	13,371	15,814
Colors and Dyes:			
Butter and cheese coloring	119,203	215,101	66,464
Colors for printing	29,469	133,700	31,215
Denmark	6,945	48,400	6,025
Finland	11,358	55,834	6,100
Norway	11,135	....	19,090
Colors prepared with oil	36,230	151,599	3,040
Dyestuffs, vegetable	3,172	29,323	3,307
Earth colors	13,574	1,598,563	922,449
Inks:			
Printer's, black	67,214	477,089	2,498
Other	179,995	149,520	99,183
Denmark	43,115	48,400	....
Finland	53,173	55,834	49,204
Germany	31,001	....	....
Norway	50,152	....	....
Russia	....	22,740	11,041
Lampblack	697,985	1,057,092	599,378
Denmark	251,574	393,658	355,159
Norway	183,974	146,275	....
Mineral colors:			
Red lead	12,615[2]	1,183,654	92,595
Finland	....	722,595	70,203
Russia, European	....	439,013	22,392
Red ocher	795,894	1,114,743	644,748
Finland	737,053	1,082,847	643,900
White lead	28,642[2]	717,419	43,982
Finland	....	298,309	....
Russia, European	....	419,110	43,541
Zinc sulfide and white baryta	11,038[2]	3,884,805	380,734
Finland	....	611,336	....
Russia, European	....	3,273,469	303,133
Zinc white	99,661	7,956,124	4,351,938
Denmark	53,627	....	22,046
Finland	....	2,234,170	1,434,877
Germany	....	167,276	....
Norway	....	26,676	752,540
Russia, European	....	5,528,001	2,142,474
Other	18,538[2]	844,170	322,350
Finland	....	337,127	211,902
Russia, European	....	44,070	107,834
Tar colors	7,315[2]	16,252	170,389
Finland	....	5,611	116,615
Russia, European	....	10,318	53,708
Varnish:			
Oil	19,217	105,195	....
Spirit	8,241	29,513	2,383
Other	82,975	309,438	89,489
Finland	32,205	37,844	....
Norway	27,053	199,056	88,918
Other colors, dyes, etc.	19,006	364,493	139,743

[1] All potassium chlorate.
[2] Not given by countries.

Exports of Chemicals and Allied Products (*Continued*)

	1913 Pounds	1916 Pounds	1917 Pounds
Oils, Fats, and Waxes:			
Acetone and acetone oil	24,233[1]	153,773	79,952
Denmark	....	8,940	20,977
Finland	....	28,825	....
Germany	....	....	34,193
Norway	....	44,749	20,587
Russia, European	....	39,939	....
Animal fat:			
Bone fat	343,640	1,055,774	....
Germany	320,871	1,055,774	....
Other	134,214	....	472,424
Germany	54,846	....	472,424
United Kingdom	76,341	....	....
Animal oils:			
Fish oils	245,837	428,177	147,146
Germany	238,639	273,121	147,146
Other	92,516[1]	319,954	466,579
Germany	....	289,354	442,827
Degras (tanner's fat)	51,865	....	....
Lubricating substances not elsewhere specified	52,943	345,293	....
Germany	....	315,745	....
Machine and wagon grease	23,084	4,032	....
Mineral oils:			
Crude	93,287	....	40,786
Refined:			
Benzine and gasoline	4,324,376	....	....
Denmark	2,521,734	....	....
Norway	1,802,642	....	....
Illuminating oils	6,758,124	3,375[1]	9,921[1]
Denmark	6,076,237	....	....
Norway	672,705	....	....
Lubricating oils:			
Light	1,122,419	32,752	....
Denmark	824,185	....	....
Norway	220,716	....	....
Dark	64,749	2,627,056	1,388,900
Germany	....	2,627,056	1,388,900
Other	22,304	1,508	....
Oilcake	4,565,740	....	....
Olein	576,465	62,507	188,496
Denmark	68,210	....	....
Finland	76,447	....	....
Germany	336,336	62,507	188,496
Paraffin	3,600	8,534	....
Resinous oils	74,319	....	....
Stearin (stearic acid)	60,278	7,727	....
Tallow	1,180,233	67,009	263,494
Denmark	318,139	....	....
Germany	579,755	66,899	263,494
Norway	264,283	....	....
Textile-dressing preparations containing soap	9,169	6,717	441
Turpentine oil	503,224	1,034,405	840,305
Denmark	....	....	190,533
Germany	301,056	898,088	649,744
United Kingdom	152,995	....	....
Vaseline	866	69,731	....
Germany	....	60,981	....
Vegetable oils:			
Fixed:			
Cottonseed	21,385	279,351	30,953
Germany	....	266,234	30,953
Hemp and castor	608	196,831	....
Germany	....	191,115	....
Linseed:			
Raw	1,585	1,828,616	....
Germany	....	1,828,616	....
Boiled	1,969	95,300	....
Germany	....	94,672	....
Maize	....	679,678	....
Germany	....	679,678	....
Olive	622	705,763	....
Germany	....	354,059	....
Russia, European	....	255,817	....
Soy bean	....	352,932	....
Germany	....	352,932	....
Turnip and rapeseed	1,179	1,832	....
Other	582,268	487,752	79,273
Denmark	374,985	....	....
Germany	158,733	402,818	79,273
Volatile	2,112	18,821	13,975
Tars, Gums, and Resins:			
Benzene oils:			
Carbolic acid, cresol, and creosote oil	6,669	11,230	....
Carbolineum	37,425	60,219	....
Naphthalene	456	497,534	45,673
Finland	....	166,747	....
Russia, European	....	330,787	....
Other	8,800	6,426	871
Caoutchouc and gutta-percha:			
Crude	439	32,483	9,691
Germany	....	32,483	9,691
Dissolved or paste	83,034	33	110
Norway	42,659	....	....
Russia, European	34,826	....	....
Coal tar	3,434,377	1,654,178	4,327,941
Finland	1,851,883	1,597,868	....
Germany	....	....	4,199,794
Norway	....	....	128,147
Russia, European	1,362,749	....	....
Coal tar prepared for covering roofs	639,945	796,784	....
Finland	560,273	425,179	....
Norway	....	187,717	....

[1] Not given by countries.

EXPORTS OF CHEMICALS AND ALLIED PRODUCTS (*Continued*)

	1913 Pounds	1916 Pounds	1917 Pounds
TARS, GUMS, AND RESINS (*Concluded*):			
Dextrin:			
Solid	3,166	17,635	88
Liquid	55,016	800,268	28,248
Denmark	....	150,305	....
Norway	....	559,170	....
Gelatin, in sheets	....	7,725	....
Glue:			
For printing cylinders	14,088	15,273	1,843
Liquid	1,847	78,642	4,806
Not liquid:			
Agar-agar	....	19,652	....
Germany	....	14,032	....
Gelatin glue	214	5,042	....
Isinglass	....	4,504	6,237
Other	72,811	212,612	....
Vegetable	2,458	1,276	....
Gum, natural	3,056	183,409	22,046
Austria	....	46,519	....
Germany	....	108,195	22,046
Pitch of coal or wood tar	305,644	3,091,043	174,911
Finland	....	1,320,101	....
Germany	....	1,470.803	114,584
United Kingdom	188,222	....	....
Resins:			
Colophony	7,083	80,503	....
Germany	....	59,537	....
Copal	66	10,518	....
Shellac	1,060	7,271	....
Other	10,957[1]	6,817,580	3,065,351
Austria	....	418,537	32,143
Finland	....	203,412	55,151
Germany	....	5,862,221	2,973.450
Hungary	....	125,038	....
Russia, European	....	134,692	....
Resin soap and tanners' glue	1,769,176	1,577,918	662,604
Denmark	844,796	....	....
Germany	194,613	1,484,185	662,604
Netherlands	113,713	....	....
United Kingdom	560,564	....	....
Rubber waste	1,396,949	1,707,046	2,715,051
Denmark	516,216	600,981	1,360,721
Germany	167,259	1,042,666	1,354,330
United States	582,180	....	....
Tar oils	1,209,159	1,406,089	508,548
Austria	....	198,533	....
Germany	202,325	933,029	364,101
Hungary	....	97,948	....
United Kingdom	891,970	37,699	8,819
Terpineol, safrol, and menthol	280	24,182	6,579
Austria	....	4,993	....
Germany	....	16,486	4,870
Hungary	....	2,381	....
Turpentine	44,357	13,676,029	5,966,499
Germany	3,448	13,573,288	5,884,684
United Kingdom	40,909	....	....
Wax (beeswax, carnauba, etc.)	5,035	13,642	82
Wood tar and tar water	17,627,605	23,630,951	15,289,016
Belgium	1,551,035	73,855	....
Denmark	1,035,935	1,798,678	1,060,078
France	4,523,220	1,212,127	....
Germany	2,416,696	9,243,978	11,293,758
Netherlands	1,903,020	3,084,579	320,589
Norway	2,441,400	5,816,257	2,404,950
United Kingdom	2,319,539	390,618	....
ORES, ETC.:	Metric Tons	Metric Tons	Metric Tons
Antimony	7	....	....
Copper	1,709	2,278	....
Graphite	48	9	3
Iron	6,439,750	5,536,641	5,818,498
Belgium	231,647	....	....
Germany	4,977,395	4,298,586	4,824,748
Norway	11.391	168,393	954,694
United Kingdom	672,836	846,222	....
United States	361,215	217,236	....
Magnesite and witherite	1,249	4,989	6,291
Mica	....	25	8
Sulfur pyrites	500	14,003	29,800
Germany	100	13,992	29,799
Zinc	46,696	9,351	6,804
Belgium	23,211	....	....
France	10,585	....	....
Germany	11,845	9,351	2,167
Netherlands	....	....	4,387
Other	4,478	1,376	549

[1] Not given by countries.

EXPORTS OF CHEMICALS AND ALLIED PRODUCTS (*Concluded*)

Articles	1913 Pounds	1916 Pounds	1917 Pounds
MISCELLANEOUS MATERIALS AND MANUFACTURES:			
Candles	78,691	9,251	....
Chalk, ground, washed or precipitated	20,921,956	13,683,679	16,687,768
Brazil	....	1,416,400	....
Finland	1,632,206	2,966,016	975,319
Germany	15,658,149	4,280,980	10,802,159
Netherlands	....	1,817.913	....
Norway	1,830,127	1,761,892	2,547,691
Explosives	316,720	1,103,579	798,600
Gases:			
Coal gas	88,609	4,916	13,625
Oxygen and hydrogen gas	118,374	650,394	2,090,243
Denmark	109,476	623,498	1,990,009
Other	623,908	833,385	454,531
Australia	39,110	114,562	65,884
Denmark	21,202	53,047	76,899
Hungary	64,617	....	....
Norway	12,035	37,240	85,027
Russia, European	22,266	223.187	20,227
United States	298,845	212,329	110,672
Glass	28,482,475	33,786,561	14,546,329
Flasks and bottles	28,464,776	31,947,928	12,809,755
Insulating material	96,032	51,048	81,919
Matches:			
Safety	61,251,599	108,967,423	85,101,694
Austria	49,604	2,779,022	150,729
British India	5,479,103	....	....
Denmark	512,371	1,129,489	2,780,307
Finland	....	1,640,632	3,727,128
Germany	7,582,208	15,525,351	6,741,327
Netherlands	1,850,343	6,073,871	7,848,713
Russia, European	....	12,010,493	25,927,946
United Kingdom	24,444,208	56,536,041	30,966,226
United States	7,286,188	2,839,439	4,722,542
Other	15,060,463	9,051,082	2,077,908
British India	6,826,511	....	....
United Kingdom	6,663,434	7,722,566	20,236,631
Paper and pulp:			
Cardboard	57,137 884	94,312,364	42,273,557
Paper	418,023.082	489,731,781	260,526,131
	Metric Tons	Metric Tons	Metric Tons
Pulp	1,009,359	1,009,163	695,948
Polishes for leather goods:	Pounds	Pounds	Pounds
Blacking	1,883	197,975	14,603
Finland	....	175,879	14,383
Wax	9,687	23,673	....
Other	156,683	235,345	3,768
Finland	....	59,709	....
Norway	....	44,912	....
Russia	101,196	106,897	....
Putty	46,731	786,724	49,919
Finland	31,034	....	....
Germany	....	759,906	22,046
Soap:			
Perfumed	31,660	80,964	4,087
Finland	22,381	39,330	....
Germany	....	34,158	....
Soft	38,329	1,401,178	690
Germany	....	1,401,178	....
Other	10,366	629,568	880
Austria	....	264,555	....
Germany	....	347,518	....
Vinegar and acetic acid in casks:			
Up to 10% acid content	1,642	72,011	38,424
Of higher acid content	210,288	43,078	259,541
Denmark	....	....	72,675
Netherlands	....	....	109,716
United Kingdom	173,586	....	....
In other containers	132,049[1]	424,826	313,258
Austria	....	103,094	105,179
Germany	....	100,029	30,459
Hungary	....	94,264	65,763
Netherlands	....	....	....
United Kingdom	....	69,235	109,652
Washing, cleansing, and polishing preparations	802,662	616,503	58,594

[1] Not given by countries.

CONTRIBUTIONS FROM THE CHEMICAL WARFARE SERVICE, U. S. A.

A METHOD FOR DETERMINING THE SULFUR MONOCHLORIDE CONTENT OF MUSTARD GAS-S_2Cl_2 MIXTURES[1]

By W. A. Felsing, S. B. Arenson and F. J. Kopp

Chemical Laboratory, Edgewood Arsenal, Edgewood, Maryland

Received May 5, 1920

In the manufacture of mustard gas (β,β-dichloroethyl sulfide) from sulfur monochloride and ethylene by the improved Levinstein process as employed at Edgewood Arsenal, the sulfur monochloride content of the reaction mixture is kept constant or is varied as is required by the rate of absorption of ethylene, the temperature, or the capacity of the cooling system. This S_2Cl_2 concentration is generally kept between 25 and 30 per cent throughout the run until all the S_2Cl_2 has been added; it is then gradually decreased until practically zero. During the entire operation it is essential that an accurate knowledge of the S_2Cl_2 content be available in order to secure the conditions for a maximum rate of absorption of ethylene and to avoid the reaction "running wild" and spoiling the entire charge. Observations of the S_2Cl_2 content were required every 20 min.; hence a quick method of determining its concentrations in the mustard gas had to be devised. If it had been possible to measure accurately the amount of ethylene absorbed, it would have been possible to calculate the S_2Cl_2 content from a knowledge of the initial charge of mustard gas and the S_2Cl_2 added. Curves which gave this information for any particular initial charge of mustard gas were constructed, but the measurement of large volumes of effluent gases of corrosive nature was not feasible; hence a quick chemical control became necessary.

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The method devised and used at the Edgewood Plant of Edgewood Arsenal is based upon the liberation of iodine from sodium iodide by means of sulfur monochloride. The data seem to establish quite firmly the fact that the liberation of iodine is in accordance with the equation

$$S_2Cl_2 + 2\ NaI = I_2 + 2\ S + 2\ NaCl \qquad (1)$$

The iodine liberated was titrated with a standard sodium thiosulfate solution, and from the data obtained the sulfur monochloride weight was calculated according to the above equation.

The only reference so far found in the literature regarding the reaction between iodides and sulfur monochloride was the work of Hautefeuille,[1] who stated that the reaction between anhydrous hydriodic acid and sulfur monochloride was quite vigorous at room temperature, yielding hydrochloric acid, free iodine, the iodide of sulfur, and finally, with an excess of hydriodic acid, hydrogen sulfide. Hautefeuille does not give any definite equations for the reactions described; but if the formation of the iodide of sulfur be regarded merely as metathetical, the equation which would probably describe his results would be

$$S_2Cl_2 + 6\ HI = 2\ HCl + 2\ H_2S + 3\ I_2. \qquad (2)$$

But if it be considered that in a water solution, as in the proposed method, hydrogen sulfide reacts with iodine to form hydriodic acid and free sulfur according to the equation

$$2\ H_2S + 2\ I^\circ_2 = 4\ HI + 2\ S^\circ \qquad (3)$$

the addition of Equation 3 to Equation 2 represents the reaction which would take place when a water solution of hydriodic acid is placed in contact with sulfur monochloride.

$$S_2Cl_2 + 2\ HI = 2\ I^\circ + 2\ S + 2\ HCl \qquad (4)$$

By inspection, it is seen that Equations 1 and 4 both call for the liberation of one molecule of free iodine for every molecule of sulfur monochloride used.

ACCURACY ATTAINABLE AND REQUIRED—The sulfur monochloride used in this investigation was prepared by carefully refluxing crude sulfur monochloride with an excess of sulfur and then distilling off the sulfur chloride from this excess. The distillate was redistilled, the fraction coming over between 137.5° and 138.5° C. being collected for use. The purified sulfur monochloride was weighed (in small tipped glass bulbs, sealed after filling), dissolved in carbon tetrachloride, and diluted to obtain weight per cent solutions ranging from 0.02 to 25 per cent S_2Cl_2.

The accuracy of the determination based upon Equation 1 is shown by the following tabular presentation of the experimental data:

Conc. Per cent	Wt. S_2Cl_2 in Sample	Wt. S_2Cl_2 Determined by Titration	Variation Gram	Error Per cent	Error in Conc. Per cent
0.02	0.03041	0.02884	—0.00157	5.16	0.001
0.04	0.03041	0.02917	—0.00124	4.08	0.002
0.10	0.03041	0.02982	—0.00059	1.80	0.002
0.20	0.03041	0.03045	+0.00004	0.14	0.000
0.40	0.03041	0.03039	—0.00002	0.07	0.000
0.80	0.06082	0.06041	—0.00041	0.67	0.005
1.00	0.03041	0.02984	—0.00057	1.87	0.019
2.00	0.03041	0.02975	—0.00066	2.17	0.043
3.00	0.22869	0.22033	—0.00800	3.50	0.105
7.50	0.22869	0.22139	—0.00730	3.19	0.239
10.00	0.44990	0.43800	—0.01190	2.65	0.265
15.00	0.44990	0.43810	—0.01180	2.62	0.393
25.00	0.44990	0.44350	—0.00640	1.42	0.355

Determinations were also made by using mustard gas as the solvent for the sulfur monochloride, in order to duplicate plant conditions. Since, however, sulfur monochloride itself reacts with mustard gas to yield chlorinated mustard gas (at a rate proportional to the S_2Cl_2 concentration), the determinations at high concentrations (20 to 30 per cent) of sulfur monochloride must be made quickly to yield accurate results. An additional source of error lies in the reaction between the sulfur monochloride and the ethylene dissolved in the reaction mixture, which again calls for a rapid determination of the S_2Cl_2 content at its higher concentrations.

The conditions of the Levinstein process are such as to require a knowledge of the sulfur chloride content with an accuracy of only about one per cent, *i. e.*, it is practically immaterial, as far as operating conditions go, whether the S_2Cl_2 is reported as 24 or 26 per cent, when it is in reality 25 per cent. The determination of the S_2Cl_2 content by this method is accurate to at least one-half per cent at the higher concentrations of sulfur monochloride (20 to 30 per cent), and to about one-tenth per cent at lower concentrations (2 to 5 per cent). An inspection of the last column of the table will serve to illustrate these statements. The method is reliable for sulfur monochloride concentrations as low as 0.04 per cent. The main factor in an accurate determination in the Levinstein plant control operations is the *time* which elapses between the drawing of the sample and its introduction into the sodium iodide solution. In view of such requirements and conditions, the following procedure has been adopted, as it yields results which are certainly made with an accuracy required by the plant operation of the Levinstein process.

METHOD OF PROCEDURE

The method is outlined in order to show under what conditions it was employed. In a glass-stoppered Erlenmeyer flask of 250 cc. capacity are placed about 25 cc. of an approximately normal solution of sodium iodide and 10 cc. of carbon tetrachloride. The flask is then weighed accurately to the second decimal place.

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[1] *Bull. soc. chim.*, [2] 7 (1867), 198.

The sample of the mustard gas-S_2Cl_2 mixture is then quickly introduced into the flask by means of a 2 cc. immersion pipet, and the flask is weighed again; this yields a sample of about 2.5 g. A known excess of a standard sodium thiosulfate solution is added, and the excess is titrated with a standard iodine solution, using starch as an indicator. It has been found that this back titration is quicker and yields more uniform results than does the single direct titration with thiosulfate solution. The number of cc. of thiosulfate solution used, multiplied by its S_2Cl_2 equivalent in grams, yields at once the S_2Cl_2 content of the sample. From these data the percentage composition of the mustard gas-S_2Cl_2 mixture can be calculated.

SUMMARY

1—The need of a chemical control of the sulfur monochloride content in the reaction mixture of the Levinstein process for mustard gas has been pointed out.

2—The availability of iodine liberation by sulfur monochloride as a means for determining the sulfur monochloride is discussed.

3—The accuracy obtainable and the accuracy required by plant operations are presented.

4—The procedure for control operations is outlined.

ACKNOWLEDGMENT

The writers wish to express their appreciation of the help and suggestions of Major Wm. Lloyd Evans, of the chemical laboratory of Edgewood Arsenal.

PRESSURES PRODUCED BY THE ACTION OF SULFUR MONOCHLORIDE UPON β,β'-DICHLOROETHYL SULFIDE[1]

By Thos. G. Thompson and F. J. Kopp

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Received May 5, 1920

The purpose of this investigation was to measure the pressures produced when relatively small concentrations of sulfur monochloride reacted with β,β'-dichloroethyl sulfide.

EXPERIMENTAL

The apparatus consisted of manometers connected with pear-shaped flasks containing varying concentrations of sulfur monochloride and β,β'-dichloroethyl sulfide. The latter substance was prepared by double vacuum distillation of the crude commercial product over calcium chloride. After the second distillation it showed a melting point of 13.6° C. The sulfur monochloride was purified by distillation at 136° to 138°.

All proper precautions were taken to see that the apparatus was absolutely dry. In sealing the flasks to the manometers, a long calcium chloride tube was used by the glass blower.

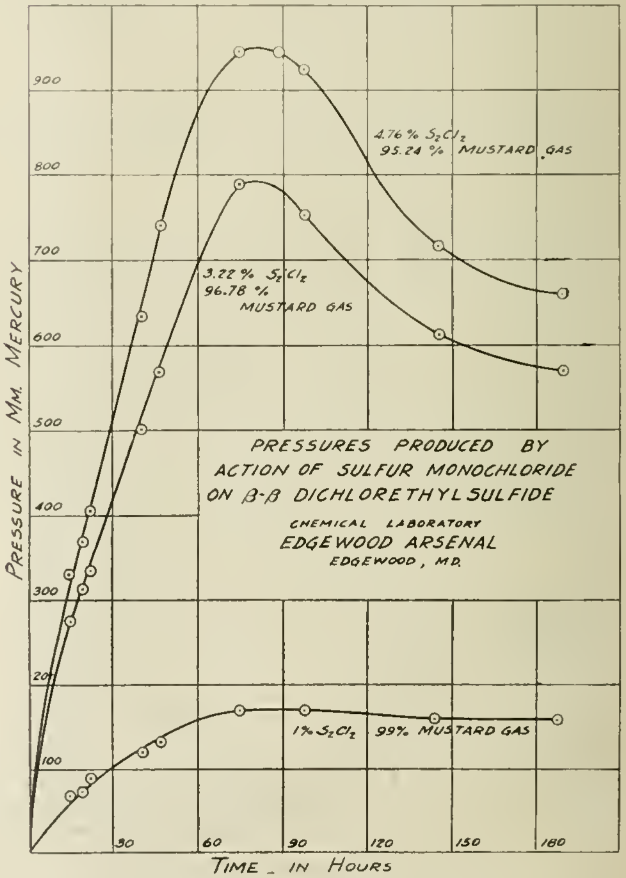
The actual volumes of the flasks, together with the portions of the tubes not filled with mercury and composing an arm of each manometer, were measured. Proper volume corrections were made for the changing of the mercury in the arms of the manometers connected with the flasks.

Four different experiments were run. In each case, the time, temperature, and barometric pressure were recorded every time readings of the manometer were made.

Expt. 1 served as a blank and was run with 50.4 g. of the pure mustard gas in the flask. The data are given in Table I. Expt. 2, the data for which are found in Table II, consisted of a mixture of 64.0 g. of the dichloroethyl sulfide with 0.64 g. of sulfur monochloride. Expt. 3 (Table III) contained 41.1 g. of the pure mustard gas (96.78 per cent) and 1.37 g. of sulfur monochloride (3.22 per cent). Expt. 4 (Table IV) consisted of 49.4 g. of the pure mustard gas (95.24 per cent) and 2.47 g. of sulfur monochloride (4.76 per cent).

TABLE I—PURE β,β'-DICHLOROETHYL SULFIDE

Time Hrs.	Temp. ° C.	Pressure Mm.	Volume N. P. T.	Decreased Volume Cc.
0	18	751	66.4	0.0
16	17	745	66.1	0.3
19	18	748	66.1	0.3
22	20	753	66.1	0.3
40	18	746	66.0	0.4
46	21	756	66.1	0.3
72	25	767	66.2	0.2
89	22	760	66.3	0.1
96	24	763	66.1	0.3
144	21	758	66.3	0.1
189	20	750	66.0	0.4



The tables show that a maximum pressure is reached in approximately 72 hrs., after which time a steady decrease is noted. In several previous experiments the same decrease in pressure had been observed at the end of 72 hrs. when rubber connections were used. Repetition of these experiments with glass-sealed joints showed that this was not due to faulty joints or action of the gases on the rubber.

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[1] Published by permission of the Chief of the Chemical Warfare Service.

Table II—1.00 Per cent Sulfur Monochloride : 99.00 Per cent β,β'-Dichloroethyl Sulfide

Time Hrs.	Temp. ° C.	Barometric Pressure Mm.	Manometer Reading Mm.	Increase Pressure Mm.	Volume N. P. T. Cc.	Increase per Unit Volume Cc.	Increase Pressure	
							Pressure V_oT_o Mm.	100 G. Mustard Gas Mm.
0	18	...	762	...	134	0	0	0
16	17	772.5	796.5	24	141	5.2	40	64.5
19	18	772.5	806	34	142	6.0	46	71.8
25	21	771	830	59	145	8.0	61	95.4
40	18	768	833	65	147	9.3	74	115.6
46	19	767	850	83	149	11.2	85	132.8
70	19	765	860	95	153	14.2	108	170
96	24	761	880	119	153	14.2	108	170
136	19	765	857	92	152	13.4	102	160
187	20	767	862	95	152	13.4	102	160

Table III—3.22 Per cent Sulfur Monochloride : 96.78 Per cent β,β'-Dichloroethyl Sulfioe

Time Hrs.	Temp. ° C	Barometric Pressure Mm.	Manometer Reading Mm.	Increase Pressure Mm.	Volume N. P. T. Cc.	Increase per Unit Volume Cc.	Increase Pressure	
							Pressure V_oT_o Mm.	100 G. Mustard Gas Mm.
0	18	...	760	0	143	0	0	0
16	17	772.5	863	90	164	14.7	112	273
19	18	772.5	884	112	167	16.8	128	312
22	20	771	907	136	169	18.2	138	336
40	18	768	960	192	182	27.2	206	502
46	19	767	995	228	187	30.8	234	570
72	25	764	1089	325	204	42.7	325	791
96	24	761	1074	303	201	40.6	309	753
144	21	760	1010	250	190	32.9	250	609
187	20	767	990	223	187	30.8	234	570

Table IV—4.76 Per cent Sulfur Monochloride : 95.24 Per cent β,β'-Dichloroethyl Sulfioe

Time Hrs.	Temp. ° C.	Barometric Pressure Mm.	Manometer-Reading Mm.	Increase Pressure Mm.	Volume N. P. T. Cc.	Increase per Unit Volume Cc.	Increase Pressure	
							Pressure- V_oT_o Mm.	100 G Mustard Gas Mm.
0	18	...	754	0	75	0	0	0
16	17	772.5	901	129	91	21.3	162	328
19	18	772	924	152	93	24.0	182	368
22	20	771	954	183	95	26.6	202	409
40	18	768	1040	272	106	41.3	314	636
46	19	767	1092	325	111	48.0	365	738
72	25	764	1220	456	121	61.3	466	944
89	22	762	1183	421	121	61.3	466	944
96	24	761	1190	429	120	60.0	456	924
144	21	760	1088	328	110	46.6	351	716
187	20	767	1053	286	107	42.6	324	656

When the apparatus was disconnected, small amounts of hydrochloric acid gas and hydrogen sulfide were detected in the gases liberated by the action of sulfur monochloride on the β,β'-dichloroethyl sulfide. Owing to the solubility of hydrogen chloride in the latter substance, the increases in pressures shown in the tables and the accompanying plot do not actually represent the total gases produced.

CONCLUSIONS

1—There is a decided interaction when small amounts of sulfur monochloride are placed in contact with large amounts of β,β'-dichloroethyl sulfide.

2—This interaction is manifested by pressures resulting from the production of gases. The maximum pressure is reached at the end of 3 days.

3—A secondary reaction takes place between the substance and the gases, as indicated by a decrease in pressure at the end of three days.

THE SOLUBILITY OF β,β'-DICHLOROETHYL SULFIDE IN PETROLEUM HYDROCARBONS AND ITS PURIFICATION BY EXTRACTION WITH THESE SOLVENTS[1,2]

By Thos. G. Thompson and Henry Odeen

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Received May 5, 1920

The question of the solubility of dichloroethyl sulfide in petroleum hydrocarbons has been investigated for the purpose of ascertaining the suitability of such solvents as agents in extracting pure mustard gas from the crude commercial product. Its marked solubility in the common petroleum hydrocarbons was quite contrary to the belief commonly accepted in April 1918.

The method employed for the study of the intersolubility of dichloroethyl sulfide and the petroleum hydrocarbons was essentially that used by Rothmund.[1]

NATURE AND PREPARATION OF MATERIALS

DICHLOROETHYL SULFIDE—The material which was used in the intersolubility experiments was obtained by double distillation at a pressure of 13 to 14 mm.

PETROLEUM HYDROCARBONS—The ligroin utilized was obtained from the commercial material by distillation. Only that portion distilling below 100° was employed. The specific gravity of the distillate at 24° C. was 1.6677. The nature of the other hydrocarbons used is illustrated by the distillation curves shown in Fig. 1.

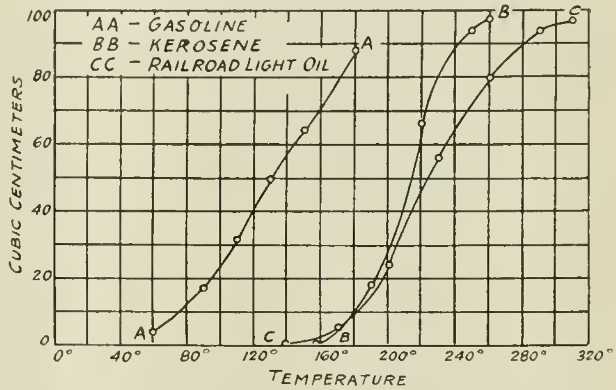

Fig. 1—Distillation Curves of Hyorocarbons Used

SULFUR MONOCHLORIDE—This was obtained by distillation of the commercial product, the portion boiling between 136° to 138° C. being utilized.

SULFUR—The pulverized C. P. rhombic modification was employed.

CHLORINATED MUSTARD GAS—This was made by the interaction of distilled dichloroethyl sulfide with sulfur dichloride in a carbon tetrachloride solution below 50° C. The addition of the dichloride solution was gradual and accompanied with constant shaking. When the product was distilled at 17 mm. pressure, the excess of sulfur dichloride and carbon tetrachloride distilled off first. The chlorinated product which came over at 112° was collected separately and used in the intersolubility experiments given in Table VI. It was of a light brown color, and its specific gravity at 22° was 1.355.

INTERSOLUBILITY EXPERIMENTS

DICHLOROETHYL SULFIDE AND LIGROIN—The results obtained from a study of the intersolubility of dichloroethyl sulfide and ligroin at various temperatures are given in Table I and illustrated by the curve AA in Fig. 2. The critical point of solubility, that is, the temperature above which the two substances would be mutually soluble in all proportions, was found to be 19° C. The highest temperature at which solid

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[1] Published by permission of the Chief of the Chemical Warfare Service.

[2] The authors wish to acknowledge the advice and suggestions given by Major Wm. Lloyd Evans and also the assistance received from Messrs. J. J. Alexander, J. H. Black, W. H. Gersdoroff, H. H. Harvey, Bruce Howard, J. L. Hutchinson, E. C. Mack, L. S. Minor, J. Parsons, G. T. Sohl, G. F. Seimers, M. C. Taylor, R. W. Tatem, D. R. Virtue, and C. J. Wernlund.

[1] *Z. physik. Chem.*, **26** (1898), 433.

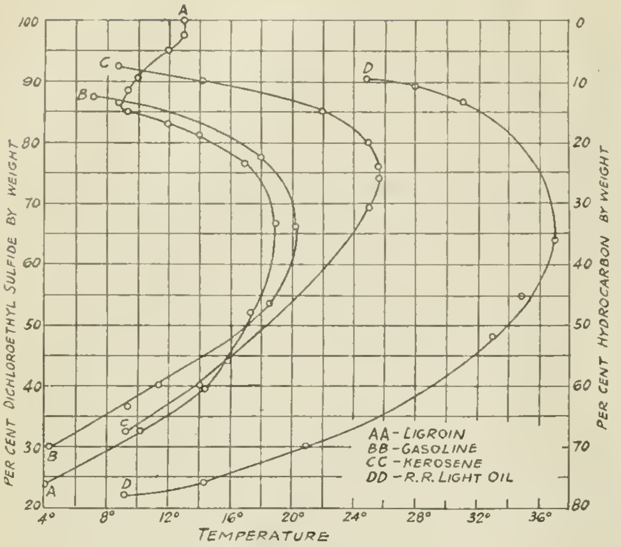

FIG. 2—INTERSOLUBILITY OF DICHLOROETHYL SULFIDE AND HYDROCARBON SOLVENTS

dichloroethyl sulfide could exist in the presence of its liquid phase and a ligroin solution of it was 8.8° C.

TABLE I

Temp. ° C.	Ligroin		Dichloroethyl Sulfide		Per cent by Weight	
	Cc.	Grams	Cc.	Grams	Ligroin	Dichloroethyl Sulfide
13.0	0	0.00	20	25.44	..	100.0
13.0	1	0.67	Constant	Constant	2.6	97.4
12.0	2	1.34	...	..	4.9	95.1
10.0	4	2.67	...	..	9.5	90.5
9.5	5	3.34	...	..	11.6	88.4
9.0	6	4.00	...	..	13.6	86.4
9.6	7	4.67	...	..	15.5	84.5
12.0	8	5.34	...	..	17.4	82.6
14.0	9	6.00	...	..	19.1	80.9
17.22	12	8.01	...	..	23.9	76.1
19.0	19	12.69	...	..	33.3	66.7
19.0	24	16.03	...	..	38.6	61.4
18.3	29	19.36	...	..	43.2	56.8
17.5	39	26.04	...	..	50.6	49.4
16.0	49	32.72	...	..	56.3	43.7
14.5	59	39.39	...	..	60.7	39.3
10.3	79	52.75	...	..	67.5	32.5
6.5	99	66.10	...	..	72.2	27.8
2.5	119	79.46	...	..	75.8	24.2
0.2	30	20.03	3.0	3.82	83.9	16.1
—2.5	Constant	Constant	2.5	3.18	86.3	13.7
—6.5	...	...	2.0	2.54	88.7	11.3
—7.5	...	. .	1.5	1.91	91.3	8.7

DICHLOROETHYL SULFIDE AND GASOLINE—The critical temperature of solubility of dichloroethyl sulfide was found to be 20.4°. The data obtained from these experiments are given in Table II and illustrated by the curve BB in Fig. 2.

TABLE II

Temp. ° C.	Dichloroethyl Sulfide		Gasoline		Per cent by Weight	
	Cc.	Grams	Cc.	Grams	Dichloroethyl Sulfide	Gasoline
7.3	20.05	25.43	5.00	3.686	87.34	12.66
18.0	Constant	Constant	10.00	7.371	77.53	22.47
20.4	...	...	17.75	13.095	66.02	33.98
18.7	...	...	30.00	22.113	53.49	46.51
14.0	...	...	40.00	29.484	46.32	53.68
9.5	...	...	60.00	44.226	36.51	63.49
4.5	...	...	80.00	58.968	30.14	69.86
7.8	15.00	19.03	3.80	2.801	87.17	12.83
13.5	Constant	Constant	30.05	22.150	46.21	53.79
9.0	...	...	45.00	33.170	36.46	63.54
4.2	...	...	60.00	44.226	30.08	69.92

DICHLOROETHYL SULFIDE AND KEROSENE—Table III shows the results secured from the study of the mutual solubilities of dichloroethyl sulfide and kerosene at various temperatures. These determinations indicate that the critical point of solubility of dichloroethyl sulfide and kerosene is 25.6°. The data given in Table III are illustrated in Fig. 2 by the curve CC.

TABLE III

Temp. ° C.	Kerosene		Dichloroethyl Sulfide		Per cent by Weight	
	Cc.	Grams	Cc.	Grams	Kerosene	Dichloroethyl Sulfide
14.2	60	48.24	25.0	31.88	60.21	39.79
9.5	80	64.32	25.0	31.88	66.87	33.13
21.9	7	5.63	25.0	31.88	15.07	84.93
24.3	9	7.23	25.0	31.88	18.58	81.42
25.6	12	9.65	25.0	31.88	23.33	76.67
25.6	13	10.45	25.0	31.88	24.79	75.21
25.6	14	11.26	25.0	31.88	26.20	73.80
25.0	18	14.47	25.0	31.72	31.33	68.67
14.3	6	4.82	33.0	41.88	10.32	89.68
8.9	6	4.82	43.0	54.47	8.12	91.88

DICHLOROETHYL SULFIDE AND RAILROAD LIGHT OIL—The results secured in these experiments are shown in Table IV and illustrated by the curve DD in Fig. 2. The critical point of solubility was found to be 37°.

TABLE IV

Temp. ° C.	Railroad Light Oil		Dichloroethyl Sulfide		Railroad Light Oil	Dichloroethyl Sulfide
	Cc.	Grams	Cc.	Grams		
25.0	2.45	1.926	14.95	18.966	9.22	90.78
28.0	5.12	4.024	25.00	31.715	11.26	88.74
31.3	3.74	2.940	14.95	18.966	13.42	86.58
37.0	13.69	10.760	Constant	Constant	36.20	63.80
35.0	20.19	15.869	...	....	45.52	54.48
33.0	26.19	20.585	...	....	52.05	47.95
23.6	38.57	30.316	...	....	61.51	38.49
20.9	56.62	44.503	...	....	70.12	29.88
14.5	75.07	59.005	...	....	75.67	24.33
9.3	87.42	68.692	...	....	78.36	21.64

From these results it is evident that with the increase in the percentage of high boiling hydrocarbons, the critical temperature of solubility for these solvents and dichloroethyl sulfide will also increase. This is very nicely illustrated by a comparison of the solubility curves shown in Fig. 2.

SOLUBILITY OF SULFUR MONOCHLORIDE IN THE HYDROCARBONS—Sulfur monochloride was found to be soluble in all proportions in ligroin, gasoline, kerosene, and railroad light oil at temperatures above 0°.

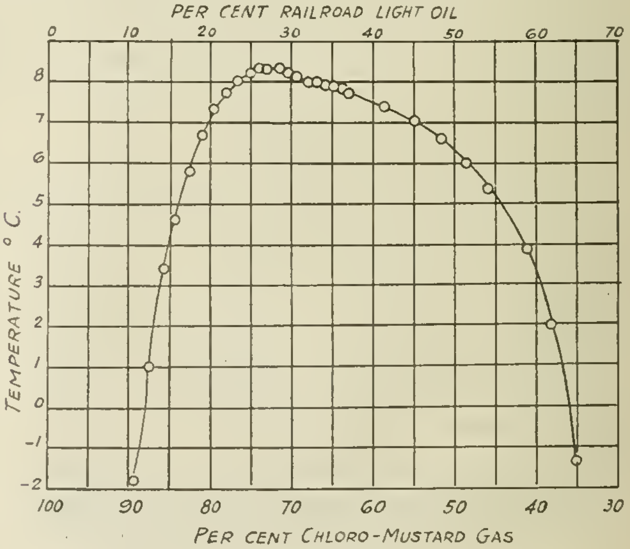

FIG. 3—INTERSOLUBILITY OF CHLORINATED MUSTARD GAS AND RAILROAD LIGHT OIL

SOLUBILITY OF SULFUR IN LIGROIN—Ligroin was shaken with powdered rhombic sulfur at 0° and at room temperature for about 6 hrs. The excess of sulfur was removed by rapid filtration. Twenty-five cc. of the filtrates were pipetted into a weighed dish and the solvent evaporated, with the results given in Table V.

TABLE V

Temp. ° C.	Sulfur in 25 Cc. Ligroin Gram	Correction (Blank)	Corrected Weight	Sulfur in 100 Cc. Ligroin Gram
0	0.049	0.001	0.048	0.192
0	0.052	0.001	0.051	0.204
24	0.085	0.001	0.084	0.336
24	0.080	0.001	0.079	0.316
24.5	0.081	0.001	0.081	0.324
28	0.092	0.001	0.091	0.364

INTERSOLUBILITY OF CHLORINATED MUSTARD GAS AND RAILROAD LIGHT OIL—The critical temperature of solubility of chlorinated mustard gas and railroad light oil was found to be 8.3°. The data obtained in these experiments are given in Table VI and illustrated in Fig. 3.

TABLE VI

Temp. ° C.	Railroad Light Oil Cc.	Railroad Light Oil Grams	Chlorinated Mustard Gas Grams	Per cent by Weight Railroad Light Oil	Per cent by Weight Chlorinated Mustard Gas
...	0	0.000	33.793	0.00	100.00
...	1	0.791	Constant	2.28	97.72
Below —2	2	1.582	....	4.47	95.53
Below —2	3	2.373	....	5.65	93.44
Below —2	4	3.164	....	8.56	91.44
—1.8	5	3.955	....	10.58	89.72
1.0	6	4.74	....	12.42	87.58
3.3	7	5.53	....	14.08	89.92
4.7	8	6.33	....	15.78	84.22
5.8	9	7.11	....	17.48	82.52
6.7	10	7.91	....	18.98	81.02
7.3	11	8.70	....	20.58	79.42
7.7	12	9.49	....	21.92	78.08
8.0	13	10.29	....	23.35	76.65
8.2	14	11.08	....	24.69	75.30
8.3	15	11.87	....	25.99	74.01
8.3	16	12.67	....	27.27	72.73
8.3	17	13.47	....	28.51	71.49
8.2	18	14.23	....	29.63	70.37
8.1	19	15.02	....	30.77	69.23
8.0	20	15.81	....	31.87	68.13
7.95	21	16.60	....	32.94	67.06
7.90	22	17.39	....	33.97	66.03
7.85	23	18.18	....	34.98	65.02
7.80	24	18.97	....	35.95	64.05
7.7	25	19.76	....	36.89	63.11
7.35	30	23.73	....	41.25	58.75
7.0	35	26.78	....	45.02	54.98
6.6	40	31.63	....	48.34	51.66
6.0	45	35.58	....	51.32	48.68
5.35	50	39.53	....	53.90	46.10
3.85	60	47.46	....	58.41	41.59
2.0	70	55.37	....	62.09	37.91
—1.4	80	63.28	....	65.18	34.82
Below —2	90	71.19	....	67.80	33.20

CONCLUSIONS FROM SOLUBILITY EXPERIMENTS

1—Dichloroethyl sulfide is soluble in the petroleum hydrocarbons and there is complete miscibility of the solute and solvent at relatively low temperatures.

2—Sulfur monochloride is soluble in all proportions.

3—Only a small amount of sulfur dissolves in the petroleum hydrocarbons.

4—Chlorinated mustard gas is soluble in all proportions of railroad light oil above 8.8°.

APPLICATION OF RESULTS—As the result of the data given above, it is self-evident that it would be highly desirable to take advantage of the following facts in a method of extracting mustard gas from the crude commercial product, using petroleum hydrocarbons as solvents.

(1) Extract the crude mustard gas at a temperature slightly above the critical point of solubility. Most of the sulfur, together with a tar-like mass, will remain insoluble.

(2) The supernatant solution is cooled considerably below the critical temperature, causing the formation of two liquid layers, the lower layer being primarily a solution of the hydrocarbon in the mustard gas. If the temperature be sufficiently lowered, solid mustard gas will precipitate out from the solution. This solid mass will retain a little of the hydrocarbon.

(3) The upper layer of hydrocarbon solvent, or that above the solid material, will contain all traces of sulfur monochloride together with chlorinated products of dichloroethyl sulfide in the crude mustard gas, and also certain amounts of dichloroethyl sulfide. The concentration of the latter will be a function of the temperature. This solvent may be used until the percentage of products other than dichloroethyl sulfide makes it undesirable.

(4) The lower layer will contain dichloroethyl sulfide and certain amounts of the hydrocarbon, the percentage of the latter being a function of the temperature.

SINGLE EXTRACTION

In order to demonstrate that such a separation as described below could be carried out, 200 cc. of crude mustard gas were shaken thoroughly with 200 cc. of ligroin in a separatory funnel at a temperature of 44° C. The mixture was allowed to cool very slowly to 25°. Three well-defined layers separated. The heaviest one consisted of a pitchy mass composed largely of sulfur. The second layer, a solution of ligroin in dichloroethyl sulfide, was drawn off in three portions and analyzed by weighing each portion and distilling off the ligroin. The amount distilled was obtained by weighing the residue. When the top layer, or the solution of dichloroethyl sulfide in ligroin, was cooled to 8°, two layers formed. The lower layer was drawn off and analyzed. The ligroin solution, or upper layer, was then cooled to —10°. The dichloroethyl sulfide precipitated in the form of long, white needles, which upon melting gave a light yellow solution containing a little sulfur. The results obtained from the analyses of the layers containing the ligroin in a solution of dichloroethyl sulfide are given in Table VII.

TABLE VII

Total Wt. of Layer Grams	Temp. of Layer ° C.	Weight Ligroin Dissolved Grams	Weight of Purified Dichloroethyl Sulfide Grams	Per cent	Melting Point ° C.	Remarks
14.8	25	0.3	14.5	5.4	..	Pitchy mass (S)
66.3	25	8.7	57.6	21.6	5.6	Dark yellow
65.2	25	8.5	56.7	21.2	4.6	Dark yellow
26.1	25	3.75	22.35	8.4	5.0	Dark yellow
80.35	8	11.05	69.3	26.0	9.0	Light yellow
59.8	—10	23.50	36.3	13.6	12.5	Light yellow

SUCCESSIVE EXTRACTION[1]

In this process a series of superimposed funnels was used. A diagram of the apparatus is shown in Fig. 4. The general method of procedure was to place equal volumes of ligroin (200 cc.) in each of the funnels. An equal volume of crude dichloroethyl sulfide (200 cc.) was then introduced in the top funnel. The contents of the first funnel were shaken, and the insoluble material which settled out from the ligroin layer was passed into Funnel 2. This passage was slow, drop by drop. As the drops came in contact with the ligroin layer in Funnel 2. they broke up into a fine spray, which scattered throughout the ligroin. The process was repeated in the succeeding funnels. Two experiments, illustrating the general results obtained by this process of extraction, gave 76.5 and 80.9 per cent of ligroin-soluble material. This soluble material was distilled *in vacuo* (2.0 to 5.0 mm.), and a yield of 86.98 per cent was obtained which showed a purity of 99.5 per cent (m. p. 13.75° C.). Better purification resulted from keeping the temperature of extraction a little below the critical point of solubility of the ligroin and dichloroethyl sulfide.

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[1] As the result of a large number of experiments with hydrocarbon solutions of mustard gas, it was noticed that the toxicity of these solutions appeared to be greater than that of either the commercial or pure mustard gas. This matter was called to the attention of the Research Division in June 1918.

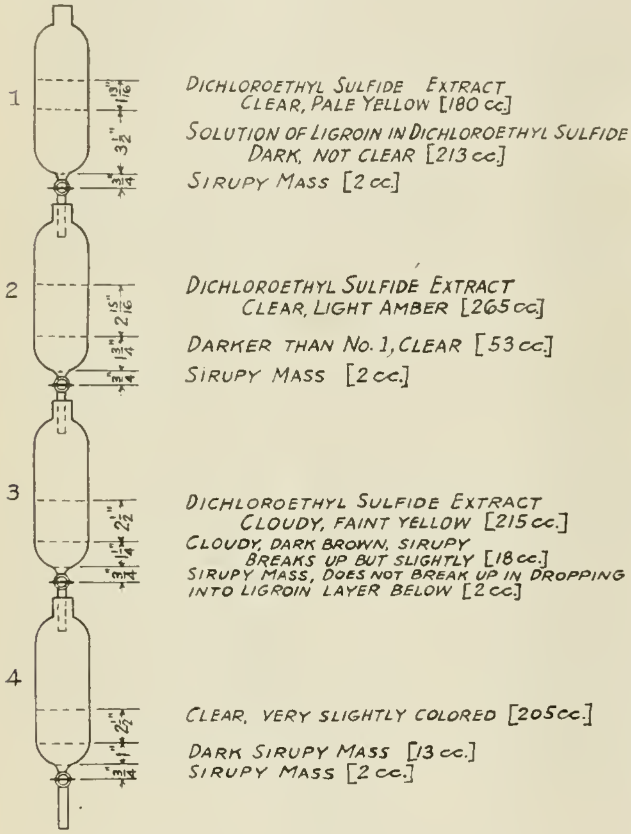
1
DICHLOROETHYL SULFIDE EXTRACT CLEAR, PALE YELLOW [180 cc.]
SOLUTION OF LIGROIN IN DICHLOROETHYL SULFIDE DARK, NOT CLEAR [213 cc.]
SIRUPY MASS [2 cc.]
1 13/16"
3 1/2"
3/4"
2
DICHLOROETHYL SULFIDE EXTRACT CLEAR, LIGHT AMBER [265 cc.]
DARKER THAN No. 1, CLEAR [53 cc.]
SIRUPY MASS [2 cc.]
2 15/16"
1 3/4"
3/4"
3
DICHLOROETHYL SULFIDE EXTRACT CLOUDY, FAINT YELLOW [215 cc.]
CLOUDY, DARK BROWN, SIRUPY BREAKS UP BUT SLIGHTLY [18 cc.]
SIRUPY MASS, DOES NOT BREAK UP IN DROPPING INTO LIGROIN LAYER BELOW [2 cc.]
2 1/2"
1 1/4"
3/4"
4
CLEAR, VERY SLIGHTLY COLORED [205 cc.]
DARK SIRUPY MASS [13 cc.]
SIRUPY MASS [2 cc.]
2 1/2"
1"
3/4"

FIG. 4—SUCCESSIVE EXTRACTION APPARATUS

The ligroin solutions when cooled to —10° gave beautiful, long, white needles, which were permitted to melt slowly after decantation of the mother liquor. Upon melting, two layers were obtained, the upper layer consisting largely of the ligroin that had been retained mechanically by the crystals. A very good product was obtained in yields varying from 51 to 63 per cent, depending upon the extent of concentration and degree of extraction. This dichloroethyl sulfide had melting points which varied from 10.4° to 10.8° C.

In all cases of extraction it was very difficult to remove the last traces of ligroin. A small amount of the hydrocarbon caused a considerable lowering of the freezing point. To determine the actual amounts of dichloroethyl sulfide contained in the various samples, distillation gave by far the more accurate results.

INSOLUBLE RESIDUE—This insoluble layer obtained from the fourth funnel in the successive extraction experiments was a thick sirupy mass and contained only traces of mustard gas. While the residues were not subjected to distillation, there was very good evidence that only very small amounts of mustard gas were present. This is found in the fact that the mustard gas dissolved in the ligroin and *vice versa*, and only a very small amount of ligroin is found in the insoluble residue. Further, this insoluble mass consists largely of sulfur, and the mustard gas is only sparingly soluble in sulfur.

ANALYSIS OF CRUDE MUSTARD GAS

The analysis of crude mustard gas used in all experiments herein reported was made as follows:

A measured volume of crude material was placed in a distilling flask of 750 cc. capacity, and the flask attached to a condenser, which was connected with a weighed receiver, and the system evacuated. The distillations were made at a pressure of 6 to 13 mm. Upon heating the distilling flask, and before any distillate was collected, there was a decided evolution of gas. While the last portion of the mustard gas was being distilled there was considerable bumping and frothing, and great care had to be manifested in completing the work. The distillate was light lemon-yellow in color. The black residue in the flask contained quantities of sulfur, was insoluble in ligroin, and dissolved in carbon tetrachloride. Table VIII gives the results obtained in two analyses.

TABLE VIII

	Sample No. 1	Sample No. 2
Weight, grams	399	261
Volume, cc.	300	200
Weight of distillate, grams	295.8	194.7
Per cent	74.17	74.6
Volume of distillate, cc.	233	157
Per cent	77.7	78.5
Weight of residue, grams	98.6	60.7
Per cent	24.65	23.3
Volatile, grams	4.6	5.6
Per cent	1.2	2.2
Freezing point of distillate, ° C.	12.0	12.7
Purity, per cent	94.2	96.5
Percentage pure mustard gas	69.9	72.0
Average Percentage	71.0	

ANALYSIS OF CRYSTALS OF DICHLOROETHYL SULFIDE OBTAINED FROM LIGROIN SOLUTION

After removing as much as possible of the ligroin retained by the crystals, they were weighed out and subjected to distillation, the results being as follows:

TABLE IX

Weight of sample, grams	313.1
Melting point, ° C.	7.4
Weight of distillate, grams	278.9
Melting point, ° C.	13.7
Purity of distillate, per cent	99.3
Per cent mustard gas in sample	89.08
Weight of residue, grams	25.7
Per cent	8.2
Weight of ligroin (by difference), grams	8.5
Per cent	2.7
Calculated as ligroin-free:	
Per cent mustard gas	90.92
Per cent residue	9.08

CONTINUOUS EXTRACTION

METHOD AND APPARATUS—In order to have a continuous process for the extraction of mustard gas from the crude material by means of ligroin, the apparatus shown in Fig. 5 was devised. The crude material flows from a separatory funnel into the main portion of the apparatus, which consists of a glass tube, about 4 ft. in length, with a bulb blown at the upper end, which serves as a settling chamber, and a stopcock at the lower end, which permits the removal of the insoluble matter. The ligroin is introduced into the apparatus by means of a long glass tube, sealed into the side of the glass column about 6 in. from the bottom. At the start the main portion of the apparatus is nearly filled with ligroin. The crude material, which enters the apparatus just below the settling chamber, is sprayed through the column of ligroin. The insoluble matter settles slowly to the bottom of the tube.

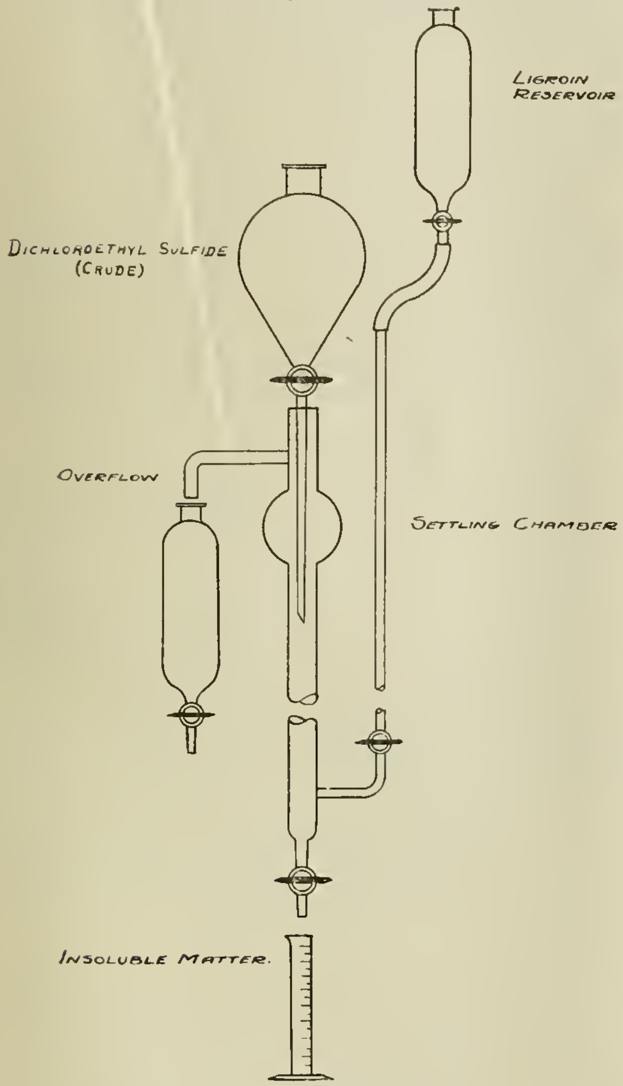

Fig. 5—Continuous Extraction Apparatus

Almost complete extraction should be assured, for, as the mass settles toward the bottom, it comes in contact with the fresh ligroin. The overflow outlet, near the top of the apparatus, consists of a tube sealed into the long glass column and bent downward at right angles so that the liquid will flow into a container placed under it. A large separatory funnel is utilized for the collection of the ligroin solution from the overflow tube. When this funnel is nearly filled it is removed and placed in a cooling bath. The insoluble matter collecting at the bottom of the apparatus is drawn off from time to time into a graduated cylinder.

EXPT. I. ABOVE THE CRITICAL POINT OF SOLUBILITY—Measured volumes of crude mustard gas and of ligroin were placed in their respective reservoirs, and the extraction carried out as described above, at temperatures varying from 25° to 27°, or several degrees above the critical point of solubility. The data are given in Table X.

Table X

Volume of ligroin used, cc.		1800
Volume accounted for, cc.		1713
Volume of crude mustard gas used, cc.		800
Volume accounted for, cc.		796
Insoluble matter at extraction temperature		
Weight, per cent	13.5	
Volume, per cent	12.3	
Insoluble matter at 16° to 18°		
Weight, per cent	17.4	
Volume, per cent	17.9	
Mustard gas crystallized		
Weight, per cent	43.7	
Volume, per cent	45.4	
Dissolved material in mother liquor		
Weight, per cent	22.7	
Volume, per cent	24.0	

EXPT. II. BELOW THE CRITICAL POINT OF SOLUBILITY—Eight hundred cc. of crude mustard gas were run through the ligroin at 15° in the continuous extraction apparatus. The insoluble matter drawn off at the bottom of the apparatus measured 745 cc. A large portion of this was ligroin which had been dissolved by the insoluble material. This residue was passed through the apparatus four times. Proper regulation of flow possibly would have increased the efficiency of extraction. The ligroin solution was placed in the freezing bath, and the mother liquor from the crystals of mustard gas was utilized in further extraction of the insoluble matter. The results obtained are given in Table XI. The weight of the insoluble matter was calculated from the data obtained in the previous experiment. It will be noted that the insoluble matter at extraction temperature in Expt. I, together with the insoluble matter at 16° to 18°, gave a total volume of 308 cc. and weighed 332 g. After the fourth extraction in this experiment (Table XI), the total insoluble material was 290 cc.

Table XI

Volume of ligroin used, cc.	1200
Volume of crude mustard gas, cc.	800
Weight of crude mustard gas, grams	1068.8
Volume of mother liquor (does not include that retained by insolubles and crystals), cc.	900
Insoluble matter, per cent	36.3
Mustard gas frozen from ligroin, per cent	51.6
Material retained by mother liquors (by difference), per cent	12.1

A portion of the mustard gas frozen out from the ligroin solution was taken for analysis after a large part of the mechanically retained ligroin had been removed by distillation. This product was distilled in a vacuum of about 13 mm., thus removing the ligroin still present. The oil bath was heated gently to 80°, and then to 95° to 100°. The data in Table XII were obtained as the result of this analysis.

Table XII

Weight of sample, grams	311.2
Weight of distillate, grams	277.8
Melting point, ° C.	13.7
Purity of distillate, per cent	99.3
Per cent of mustard gas in sample	88.64
Weight of residue, grams	25.1
Per cent	8.0
Weight of ligroin (by difference), grams	10.2
Per cent	3.4
Per cent mustard gas (calculated on ligroin-free sample)	92.2

CONTINUOUS EXTRACTION OF CRUDE MUSTARD GAS WITH KEROSENE AND RAILROAD LIGHT OIL ON A SEMI-COMMERCIAL SCALE

The object of the following experiments was to confirm the results of those carried out in glass apparatus on a laboratory scale and at the same time to simulate as closely as possible the conditions which would obtain in plant operation. The crude mustard gas was manufactured at the Edgewood Plant of Edgewood Arsenal on August 29, 1918. It had a melting point of 8.5°, was black in color, and on analysis by distillation showed 70 per cent pure mustard gas.

APPARATUS AND METHODS—To minimize danger as much as possible the apparatus was set up in an improvised laboratory out of doors. The extractor was an all-lead column with a brass valve at the bottom, and of the same essential design as the glass extractor. Its principal parts consisted of a 1.5 in. (inside diameter) lead pipe, with enlarged sections at the top and the bottom. These sections were used as settling chambers and gave the apparatus proper a length of 4 ft. A three-eighths inch vertical pipe, attached just above the lower settling chamber, was of sufficient length to furnish a pressure head which would cause a counter current to flow through the apparatus when in operation. The crude mustard gas was admitted through another vertical lead pipe entering at the top of the upper settling chamber and terminating at the center of the 1.5 in. lead pipe, about 2 in. below the bottom of the settling chamber. A three-eighths inch heating pipe, through which steam was passed when extracting at a higher temperature, ran throughout the length of the apparatus. A thermometer well was placed in the top of the apparatus in order to measure the temperature of the effluent as it left the overflow pipe. The apparatus had a volume of 7.5 liters. The accessories, such as containers, funnels, crystallizing vessels, etc., were of glass.

The extractor was operated by running about 4 liters of kerosene into the apparatus. The kerosene supply was then turned off and the material to be extracted was run in at a definite rate of flow. As soon as the extract came through the overflow pipe, the kerosene was again permitted to flow through the apparatus. The insoluble matter was drawn off at the bottom of the extractor from time to time.

EXPT. I—This and the following experiments were carried out in much the same manner as already described for continuous extraction.

The extract and the insoluble residue were run into tared bottles, and weighed. The bottle containing the extract was refrigerated at about —15° for 3 hrs., after which time large needle-like crystals formed a compact mass throughout the liquid. During the refrigeration two liquid phases settled out, the lower one black in color and very rich in mustard gas, and the upper orange in color and low in its mustard-gas content. The crystals were permitted to melt and the two liquid layers which formed were separated and weighed. Each layer was refrigerated as before and the remaining liquid drained from the crystals, the weights of which were determined. A second, third, and fourth fraction of crystals were obtained from the lower layer on further crystallization. The upper, or kerosene layer, yielded only one fraction. In draining off the mother liquor from the crystals the bottles were simply held in an inverted position for a few minutes. The data are given in Table XIII.

EXPT. II—This experiment differed from Expt. I in that the rate of flow of mustard gas was slower in order to insure more complete extraction. The results are given in Table XIII.

EXPT. III—This experiment was exactly like Expt. I, excepting that the rates of flow of the crude mustard gas and the kerosene were much slower, and the temperature of extraction was higher. The kerosene used in this experiment was obtained from the mother liquors of the two previous experiments. The data obtained are included in Table XIII.

TABLE XIII

	Expt. I	Expt. II	Expt. III
Temperature of extraction, ° C.	23–26	26–40	50–60
Rate of flow			
Mustard gas per minute, cc.	77	47	50
Kerosene per minute, cc.	125	125	83
Mustard gas used			
Weight, kilos	11.9	11.5	11.9
Volume, liters	9.0	8.75	9.0
Melting point, ° C.	8.5	8.5	8.5
Specific gravity (30°)	1.315	1.315	1.315
Kerosene used			
Weight, kilos	14.0	15.2	12.55
Volume, liters	17.5	19.0	14.75
Specific gravity (30°)	0.800	0.800	0.800
Kerosene layer			
Weight, kilos	16.44	18.27	12
Specific gravity (30°)	0.862	0.862	0.862
Per cent mustard gas crystallized	11.9	10.1	18.9
Weight, kilos	1.95	1.84	2.31
Melting point, ° C.	...	11.6	9.6
Specific gravity (20°)	...	1.192	1.216
Recrystallization, per cent	...	9.9	..
Weight, kilos	...	1.8	..
Melting point, ° C.	...	11.8	..
Specific gravity	...	1.210	..
Sp. gr. of mother liquor	0.850	0.850	0.870
Insoluble residue			
Weight, kilos	7.16	1.5	2.16
Per cent	61.2	13.2	18.2
Specific gravity (20°)	...	1.251	1.246
Mustard gas layer			
Weight, kilos	3.30	6.64	7.66
Melting point, ° C.	6.6	6.3	6.5
Specific gravity	1.221	1.209	1.244
Per cent crystallized	84.3	82.5	68.3
Melting point, ° C.	8.6	7.7	7.1
Specific gravity (20°)	1.244	1.247	1.252
Per cent recrystallized	98.4	96.0	..
Melting point, ° C.	9.5	9.5	..
Specific gravity (20°)	1.246	1.248	..
Summary			
Mustard gas from kerosene, kilos	1.40	1.13	2.50
Mustard gas from mustard layer, kilos	2.79	5.47	5.23
Total from both layers, kilos	4.19	6.60	7.73
Per cent yield	35.8	58.1	65.0

Analysis of the layers or crystals by means of distillation is practically impossible, owing to the fact that a very large portion of the kerosene boils at the same point as does the mustard gas.

PRACTICAL TESTS

A large amount of crude mustard gas was extracted with railroad light oil. The purified product, which contained railroad light oil, was placed in twelve 75 mm. shells. When these shells were exploded no flash resulted, showing that the hydrocarbon did not take fire. At the time of explosion a white cloud of smoke was produced.

CONCLUSIONS

1—The critical temperatures of solubility of dichloroethyl sulfide with the various hydrocarbons are as follows:

Ligroin	19°
Gasoline	20.4°
Kerosene	25.6°
Railroad Light Oil	37°

2—The critical temperature of solubility increases with the increase in the percentage of the more complex hydrocarbons.

3—The critical temperature of solubility of chloromustard gas is considerably below that of dichloroethyl sulfide.

4—Dichloroethyl sulfide can be extracted from the crude material, containing 71 per cent, to give yields varying from 54 per cent to 69 per cent.

DECOMPOSITION OF AND PRESSURE DEVELOPED BY MUSTARD GAS IN STEEL SHELL AT 60° C.[1]

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Received July 14, 1920

It has been determined qualitatively that crude mustard gas (dichloroethyl sulfide) slowly attacks iron, and that it is itself slowly decomposed at room temperatures by contact with iron. Since hydrochloric acid is one of the products of this decomposition of mustard gas, and since mustard gas as commercially produced is never quite dry, the effect of the decomposition is essentially a corrosion of the iron by the hydrochloric acid with liberation of hydrogen. Since the plant of Edgewood Arsenal was loading steel shell with crude mustard gas for shipment overseas, it became highly desirable to ascertain:

(1) The extent of decomposition of the mustard gas in the steel shells during a two weeks' journey in cargo vessels, at temperatures as high as 50° C.

(2) The maximum pressure that would obtain inside of the shell, in order to make provisions for a sufficiently tight or leakproof booster-shelljoint, and to provide boosters with sufficient wallthickness to prevent caving in.

Steel shell filled with mustard gas were therefore kept at 60° C. for a period of 2 wks., in order to determine the rate of decomposition and to measure the pressures developed.

The mustard gas shipped was prepared by two processes, both based upon the interaction of sulfur monochloride and ethylene. The one (the original process, designated in this paper as Process A) employed no initial charge of mustard gas as catalyzer, was operated at 60° C., and employed lead-lined reactors; the other (the Levinstein process, designated as Process B) maintained a 70 to 75 weight per cent concentration of mustard gas throughout the run until all the sulfur monochloride had been added, was operated at 30° to 35° C., and employed simple iron reactors. The products differed considerably in color, purity, amount of sulfur held in colloidal solution, acidity, etc. Both kinds of crude mustard were investigated. The vast majority of the gas, however, was prepared according to Process B.

METHODS OF INVESTIGATION

In order to gain information on the two points stated in the beginning of this paper, two series of experiments were made. The methods may be outlined as follows:

SERIES 1—Three hundred cc. samples of analyzed crude Process A and Process B mustard gas were placed in several 75 mm. shell. The shell were tightly closed by means of rubber stoppers and were kept in a thermostat at 60° C. (±1°) for a period of 16 days for the Process B samples, and 8 days for the Process A samples. A test sample was taken every two days in the order of shell number, two successive samples being taken from each shell. Two shell contained crude Process A and four shell Process B mustard gas, both of excellent quality initially. To detect any abnormal behavior during the testing period, a final sample was taken from each of the first four shell at the end of 16 days for the determination of acidity and final melting point.

SERIES 2—Three hundred cc. samples of analyzed crude Process B mustard gas were placed in 75 mm. shell connected with mercury manometers. Also, samples of Process B mustard gas which had been treated with gaseous ammonia (this procedure precipitating out about 7 to 8 per cent of the colloidal sulfur and destroying the HCl per cent) and of Process A mustard gas in which gas oil had been substituted for colloidal sulfur (by the process of extraction) were also placed in shell similarly arranged. As a check, samples of each material were placed in glass containers, producing the same void as in the steel shell, and connected to mercury manometers.

Table I—Progressive Decomposition of Mustard Gas in Steel Shell

Sample	Shell No.	Days in Shell	Melting Point (Crude) ° C.	Melting Point Lowering (Crude) ° C.	Relative Purity of Mustard Gas. Per cent	Drop in Percentage Purity	Per cent Acidity as HCl	Increase in Acidity
Process B	..	0	8.00	....	81.8	...	0.160	...
	1	2	7.90	—0.10	81.5	0.3	0.180	0.020
	1	4	7.50	—0.50	80.3	1.5	0.382	0.222
	2	6	7.20	—0.80	79.4	2.4	0.417	0.257
	2	8	7.05	—0.95	79.0	2.8	0.639	0.479
	3	10	7.10	—0.90	79.1	2.7	0.910	0.750
	3	12	6.95	—1.05	78.7	3.1	0.645	0.485
	4	14	6.10	—1.90	76.1	5.7	1.387	1.227
	4	16	6.00	—2.00	75.7	6.1	1.535	1.375
Process A	..	0	10.30	....	88.9	...	0.270	...
	5	2	9.40	—0.90	86.1	2.8	1.028	0.758
	5	4	9.20	—1.10	85.5	3.4	1.308	1.038
	6	6	9.60	—0.70	86.8	2.1	0.968	0.698
	6	8	9.40	—0.90	86.1	2.8	1.009	0.739

Zero readings were taken on each manometer at 30° C., the temperature of the bath when the manometers were sealed on. All connections had been tested for leaks. The temperature of the thermostat was raised to 60° C. and maintained at this temperature (± 1° C.) for over 10 days. An initial pressure reading was made one hour after the thermostat had been adjusted to 60° C. Subsequent manometer readings were made twice daily (at 8:30 A.M. and 4:30 P.M.).

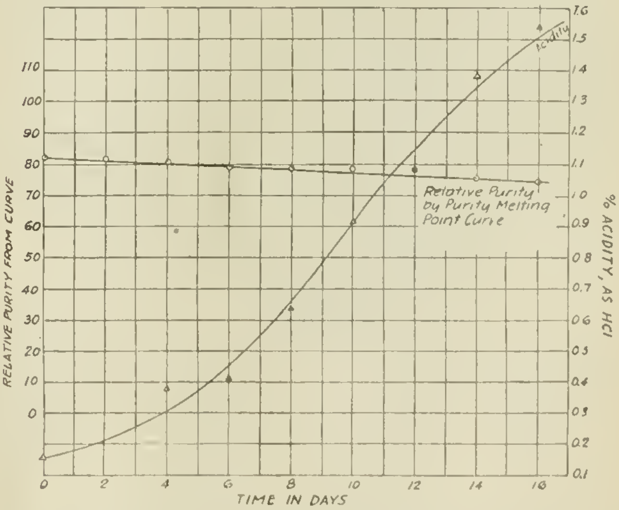

Fig. 1—Relative Purity and Acidity as a Function of Time

METHODS OF ANALYSIS

The tests for the determination of the progressive decomposition consisted of vacuum distillations, melting-point determinations on the crude and the distilled samples, and acidity determinations. The percentage purity of the distilled product and the relative percentage purity of the crude were gaged by an empirically determined purity-melting point relation.[1] Acidity determinations were made by adding chloroform (to dissolve the mustard gas) and water, and titrating with a standardized sodium hydroxide solution.

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[1] Published by permission of the Chief of the Chemical Warfare Service.

In Series 2, melting-point, acidity, and purity tests were made only at the beginning and at the end of the 10-day period.

TABULATION OF RESULTS

The results obtained in Series 1 are presented in Tables I and II; in Fig. 1 are presented the melting-point lowerings and acidity increases as related to time in days, and in Fig. 2 the relation of melting-point lowering to acidity increase. The results of the analysis of initial and final materials of the shell of Series 2 are presented in Table III. Net decomposition pressures were obtained by subtracting initial readings at 60° C. from final readings at 60° C. The thermostat temperature was lowered to 30° C. at the end of the test period, and pressures were again read. Fig. 3 gives the total pressures corrected to initial barometer and initial zero readings on manometers. Fig. 4 gives the same relation of pressure with respect to time with the additional correction for thermal expansion from 30° C. to 60° C. The lowering of pressure due *solely* to gas absorption on cooling to 30° C. is shown in Fig. 3 by the dotted lines at the end of each curve.

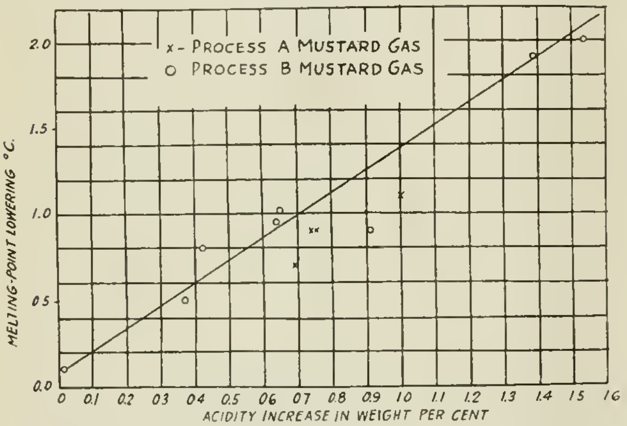

FIG. 2—MELTING-POINT LOWERING AS A FUNCTION OF ACIDITY INCREASE

TABLE II—MELTING POINTS AND ACIDITY OF MUSTARD GAS AT END OF 16-DAY PERIOD

SAMPLE	Shell No	Melting Point ° C.	Total M.-P. Lowering ° C.	Acidity	Total Increase in Acidity
Process B	..	8.0	...	0.160	...
	1	4.5	3.5	2.930	2.770
	2	5.0	3.0	1.907	1.747
	3	5.8	2.2	0.885	0.725
	4	6.0	2.0	1.535	1.375
Process A	..	10.3	...	0.270	...
	5	7.7	2.6	4.690	4.420
	6	8.9	1.4	1.862	1.592

Table II presents the results of determinations of the melting point and the acidity on the residual mustard gas in the shell of Series 1 at the end of 16 days.

TABLE III—ANALYSIS OF ORIGINAL AND FINAL MUSTARD GAS IN PRESSURE DEVELOPMENT TESTS (AT END OF 10 DAYS)

SAMPLE	Melting Point ° C.	Melting-Point Change	Relative Purity Per cent	Change in Purity	Per cent Acidity, as HCl	Increase in Acidity
Original Crude Process B	8.0	...	82.4	...	0.175	...
Process B from steel shell	6.4	—1.6	76.5	—5.9	2.040	1.865
Process B from glass container	7.6	—0.4	81.2	—1.2	0.456	0.281
Process B, ammonia-treated	8.1	...	82.7	...	0.005	...
Ammonia-treated, from shell	8.1	±0.0	82.7	±0.0	0.422	0.417
Ammonia-treated, from glass container	8.6	+0.5	84.4	+1.7	0.012	0.007
Original Sample Process A + 12 per cent oil	7.9	...	82.1	...	0.073	...
Process A + 12 per cent oil, from shell	7.2	—0.7	80.0	—2.1	0.661	0.588

DISCUSSION OF RESULTS

The data obtained in Series 1 offer substantial proof of a progressive decomposition of mustard gas in steel shell at temperatures near 60° C. This time-relative purity relation for Process B mustard gas is practically a linear function (see Fig. 1). The increase of acidity with time in the closed steel shell is also presented in the figure, showing practically a uniform rise. An increase in acidity goes hand in hand with a lowering of melting point and a decrease in actual mustard gas content. This is shown in Fig. 2.

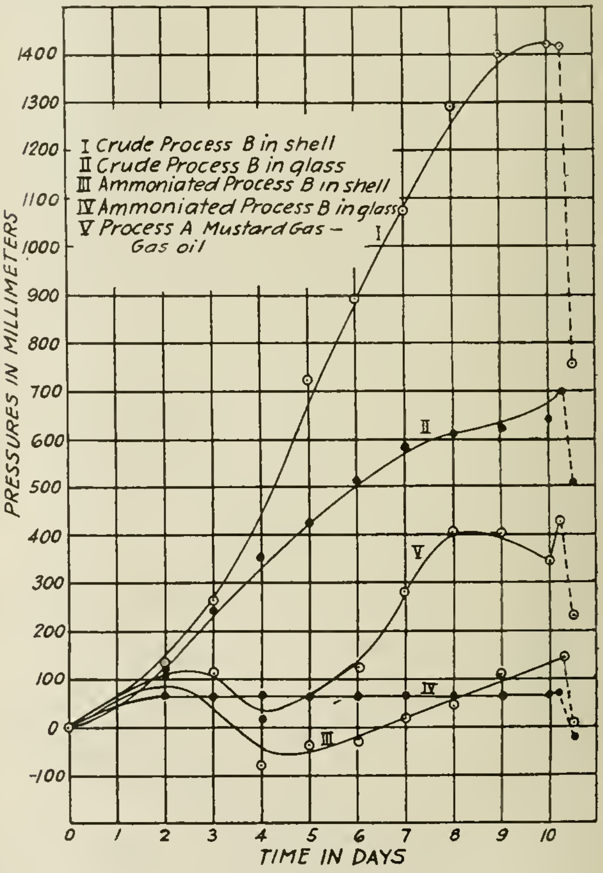

FIG 3—DECOMPOSITION PRESSURE OF MUSTARD GAS AT 60° C. (Not Corrected for Thermal Change)

The Process A mustard gas tests were continued over a period of only 8 days, and though the results are not as concordant as those on Process B mustard gas, the decomposition and the increase in acidity proceed in the same general way as for Process B.

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[1] Bureau of Mines, *Organic Report* **28**, April 6, 1918.

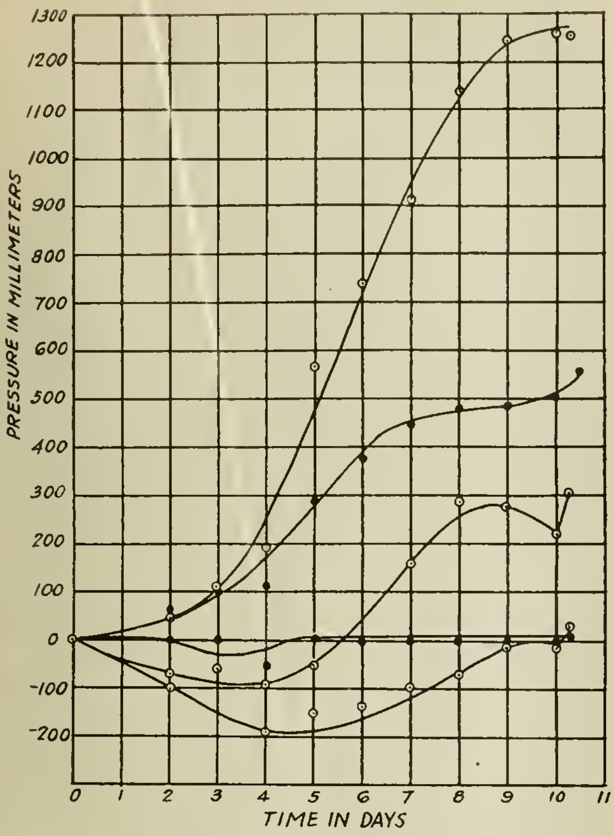

Fig. 4—Decomposition Pressure of Mustard Gas at 60° C.
(Corrected for Thermal Change)

Analysis by means of vacuum distillation does not yield satisfactory results, because the amount of sulfur precipitated out of colloidal solution varies with the time, and hence the analysis of the supernatant liquid is not a true criterion of the purity of the sample. Further, an actual decomposition of the mustard gas may be counterbalanced by a precipitation of sulfur, the precipitated sulfur adhering to the sides of the shell. The reliable criterion for determining the extent of decomposition was the melting-point determination on the undistilled mustard; since in this determination the colloidal sulfur does not affect the melting point, while the decomposition products do. Hence, a relative purity based upon these melting points is recorded, and the results given graphically in Fig. 1.

In Series 2, the relation of melting-point lowering and total acidity is again confirmed; while the relation is not the same quantitatively, the general behavior and trend is the same. The deviation may be due to several causes, but it would be idle curiosity to attempt to make an explanation.

By reference to either Figs. 3 or 4, it will be noted that a maximum pressure development is attained in about 9 days with crude Process B mustard gas. With the ammonia-treated mustard gas a negative pressure actually obtained for 3 days, after which a slight positive pressure was built up. The negative pressure is very likely the result of the neutralization of the ammonia in solution and as a gas by the hydrochloric acid formed by hydrolysis. It is possible that if the tests had extended over a longer period, a pressure as high as with the crude mustard gas would have been obtained. The pressure developed by the ammonia-treated mustard gas in glass is practically nil, and the acidity developed is very slight.

The gas oil-mustard gas mixture in general shows a behavior similar to that of the ammonia-treated materials for the earlier part of the test. However, the pressure soon develops more rapidly and would undoubtedly reach a maximum sooner.

All samples of mustard gas in steel uniformly turned deep black, while the samples in glass remained orange-yellow. (A sample of crude Process B mustard gas, which was a light orange-yellow originally and which was sealed up in a glass tube, turned a deep black after about 16 mo. A sample of pure, colorless mustard gas, however, was still perfectly clear even after 20 mo.)

CONCLUSIONS

1—A decomposition of both Process A (original 60° C. process) and Process B (Levinstein) mustard gas takes place in steel shell at 60° C. The extent of the decomposition is not serious even under the severe conditions of the investigation.

2—Sulfur is deposited in solid form in shell in amounts ranging from 5 to 8 per cent of the liquid content of the shell.

3—The pressure developed in the ordinary steel shell is at most barely two atmospheres in any one shell. This seems to be a maximum or equilibrium pressure, reached after about 9 days.

4—The acid content increases considerably, but the concentration is not sufficiently high to cause serious corrosion.

5—A preliminary treatment of the mustard gas with ammonia gas serves to delay the formation of pressure. This delay is of sufficient length to warrant the preliminary treatment of mustard gas which is to be stored for some length of time in steel shell or containers.

ACKNOWLEDGMENT

The authors desire to thank Major Wm. Lloyd Evans of the Chemical Laboratory, Edgewood Arsenal, for the timely suggestions he has given.

THE PRECIPITATION OF SULFUR FROM CRUDE MUSTARD GAS BY MEANS OF AMMONIA[1]

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Received August 19, 1920

Mustard gas (β,β'-dichloroethyl sulfide) was produced at Edgewood Arsenal by two processes based upon the interaction of liquid sulfur monochloride and ethylene gas. The following equation represents, in brief, the most probable reaction:

$$2C_2H_4 + S_2Cl_2 = (ClC_2H_4)_2S + S$$

The equation, as written, does not indicate the formation of the intermediate compound $ClC_2H_4.S.Cl$ or of the disulfide $S(C_2H_4)_2S$, both of which have been proved to be present in crude mustard gas. An inspection of the equation, however, indicates that one atomic weight of free sulfur is formed for every molecular weight of mustard gas produced. Of the total weight of the mustard gas-sulfur mixture, the sulfur constitutes 16.76 per cent.

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[1] Published by permission of the Chief of the Chemical Warfare Service.

This sulfur does not precipitate out quantitatively during the course of the reaction. During one process of manufacture (Process A, the 60° C. process) varying percentages (2 to 8) precipitated out in the form of a slimy, amorphous sludge—the greater the moisture content of the ethylene used, the greater the sulfur precipitation. During the other process (Process B, the 30° to 35° C. Levinstein process) none of the sulfur precipitated out when the ethylene gas was reasonably dry. The mustard gas produced by Process A had a marked tendency to precipitate out sulfur on standing, the amount remaining in the mustard gas being about 6 to 8 per cent by weight of the original crude, *i. e.*, about 50 to 60 per cent of the sulfur finally precipitated out, the other remaining in the mustard gas indefinitely. Lowering of the temperature (complete solidification) had the same effect, as far as quantity of sulfur precipitated was concerned. However, in the Process B mustard gas, the sulfur had but an extremely small tendency to separate out as free sulfur; in fact, most of the material produced with dry ethylene showed only a slight sulfur precipitation after a period of a month (a sample kept for 22 mo. in a sealed glass container showed only about a 1 per cent precipitation). Freezing of the sample also did not cause sulfur precipitation; repeated freezing and remelting of a sample of the crude Levinstein mustard gas had no effect on the sulfur "hold-up."

During the course of some experiments with Process A mustard gas to remove the hydrochloric acid produced by the hydrolysis of sulfur monochloride and of mustard gas, Venable and Felsing[1] bubbled moist ammonia gas through crude mustard gas. Immediately crystalline sulfur was deposited in amounts ranging from 5 to 10 per cent of the weight of the mustard gas-sulfur mixture. *Dry* ammonia passed through *dry* mustard gas had no such effect. The melting point of the ammonia-treated mustard gas was never higher, practically always the same, and occasionally slightly lower than before treatment. With the object of ascertaining the effect of ammonia gas upon the crude Process B mustard gas, in which the sulfur hold-up was complete, the following samples were subjected to a uniform ammonia treatment. Moist ammonia gas was passed through the mustard-gas sample for 5 min. The sulfur immediately began to crystallize out. After cooling, the liquid and crystals were allowed to stand in contact for 6 hrs., and the mustard gas was then filtered through a tared Gooch filter. The precipitate, consisting of sulfur and a very small quantity of ferric hydroxide, was washed free of adhering mustard gas with CCl_4 (saturated with sulfur at room temperature). The Gooch was dried at 100° C. and weighed. The ferric hydroxide was then removed with dilute sulfuric acid, and the Gooch reweighed after drying. The following table presents the data obtained:

SAMPLE	Melting Point before Treatment ° C.	Melting Point after Treatment ° C.	Pure Mustard-Gas Content Per cent	Per cent Sulfur Precipitated	Per cent Efficiency of Precipitation
1	9.2	9.20	68.2	6.79	40.50
2	8.7	8.65	71.6	6.54	39.00
3	7.8	7.80	71.5	7.44	44.35
4	7.0	6.90	69.4	7.00	41.72
5	7.4	7.40	64.5	7.10	42.35
6	8.0	8.05	70.0	6.45	37.46
7	8.2	8.10	71.7	7.80	46.50
8	7.2	7.20	71.0	7.20	42.93

In each of the samples described above, *no* sulfur had precipitated out before treatment. The mean weight per cent of sulfur precipitated out was 7.04, which means that only 42 per cent of the supposedly free sulfur was precipitated by the ammonia treatment. The melting points of the samples after treatment were practically the same as before treatment. The pure mustard-gas content was determined on the crude material before treatment by vacuum distillations and melting-point determinations on the distilled product.

From the foregoing observed facts and tabulated data, it is evident that part of the sulfur, at least, is present in the mustard gas as colloidal sulfur, since its removal does not materially influence the melting point of the mustard gas, *i. e.*, does not cause a raising of the melting point, which it would have done if the sulfur had been in true solution. Of course, there is the possibility that the sulfur existed in the mustard gas as a compound, but it is hardly probable that this compound would have the same melting point as the mustard gas. It is also quite apparent that part of the sulfur is present in the form of compounds, since by no agency whatsoever has it been possible to separate all the 16.76 per cent sulfur as such from the body of liquid, without resorting to a vacuum distillation. The sulfur, then, which is in colloidal form in crude Process B mustard gas, is about 40 to 45 per cent, while 55 to 60 per cent are present in the form of compounds.

SUMMARY

1—When mustard gas is produced from sulfur monochloride and ethylene, only part of the free sulfur formed separates out.

2—In some cases moisture, freezing, and long standing cause a partial separation of the sulfur.

3—The addition of moist ammonia causes a precipitation of about 40 to 45 per cent of the total supposedly "free" sulfur.

4—It is pointed out that the observed facts seem to indicate that part of the sulfur is present in the colloidal state, while the other part (55 to 60 per cent) seems to be present in the form of compounds.

ACKNOWLEDGMENT

The authors desire to thank Major Wm. Lloyd Evans of the Chemical Laboratory, Edgewood Arsenal, for the timely suggestions he has given.

THE INTERSOLUBILITY OF CHLOROPICRIN AND WATER[1]

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Received May 5, 1920

SOLUBILITY OF CHLOROPICRIN IN WATER

Chloropicrin was shaken with a large amount of distilled water to form an emulsion. The mixture was permitted to stand for 3 days at room temperature in order to allow the chloropicrin to settle. The water solution was then maintained at 25° C. for 6 hrs., and 100 cc. samples were analyzed by the method described below.

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[1] Cleveland Laboratory, Edgewood Arsenal Report, June 18, 1918.

[1] Published by permission of the Chief of the Chemical Warfare Service.

The solubility of chloropicrin in water at 0° was determined by shaking thoroughly and standing for several days in a thermostat at 0°. Samples of the clear solution were treated by the method given below. If portions of this solution were brought to room temperature, a decided precipitation of chloropicrin resulted. Upon cooling, the emulsion would disappear and the solution again become clear.

The solubility at 75° C. was obtained by putting the 0° solution for 2 days in a thermostat maintained at 75° to 76°. The flask holding the solution was stoppered in order to prevent evaporation.

METHOD OF ANALYSIS FOR CHLOROPICRIN IN WATER[1]—Fifty cc. of alcoholic sodium sulfite were added to each sample. (This solution was prepared by dissolving 10 g. of hydrated sodium sulfite in 250 cc. of water and diluting with an equal volume of ethyl alcohol.) The sample was refluxed with an air condenser to eliminate alcohol, the refluxing being continued until all but 10 cc. of the solution had evaporated. It was then diluted to 100 cc., and a standard solution of silver nitrate added in excess, together with 10 cc. of nitric acid. After boiling to expel the nitrous fumes and to coagulate the silver chloride, the solution was cooled and the excess silver nitrate titrated with a standard solution of ammonium thiocyanate, using ferric alum as an indicator.

TABLE I

	Temperature ° C		
	0	25	75
Grams chlorine in 100 cc. H_2O	0.1472	0.1060	0.0739
	0.1465	0.1048	0.0753
	0.1468	0.1049	0.0695
	...	0.1049	0.0674
	...	0.1042	0.0796
	...	0.1055	0.0768
	...	0.1045	0.0674
Average equivalent chloropicrin	0.2272	0.1621	0.1141

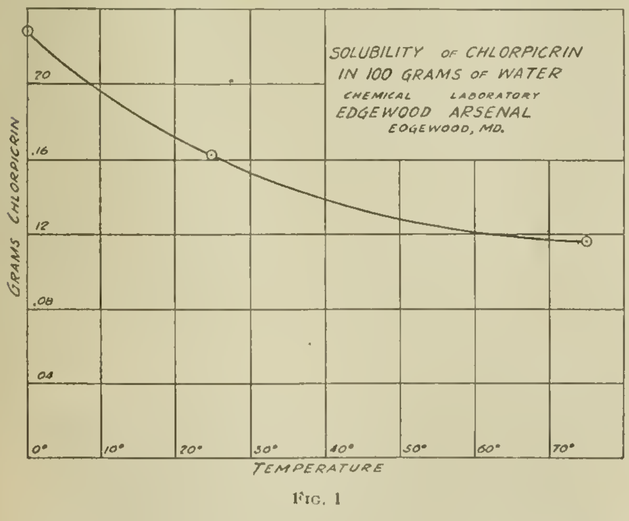

FIG. 1

Table I gives the results obtained by the analysis of the chloropicrin dissolved in water at various temperatures. The data are illustrated by the curve in Fig. 1.

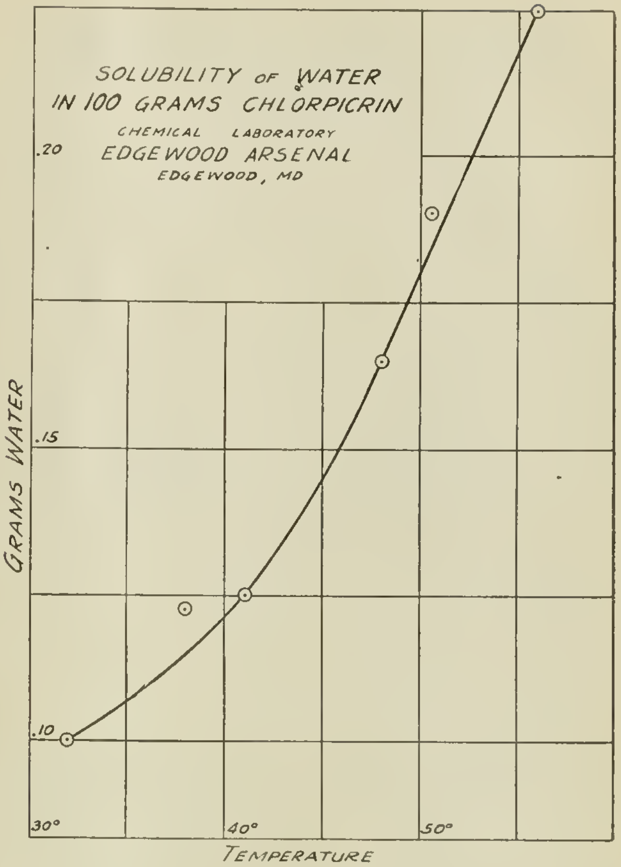

FIG. 2

SOLUBILITY OF WATER IN CHLOROPICRIN

The apparatus consisted of a glass cylinder, sealed at one end and fitted at the other with a two-hole rubber stopper. A thermometer was placed in one hole of the stopper and a small glass tube, the length of the stopper, in the other. Through this tube was introduced a glass stirring rod with a loop at one end. Chloropicrin was placed in the apparatus and very small portions of water introduced. The mixture was slowly heated and constantly stirred until all the water had gone into solution. The apparatus was then cooled and the temperature noted at which a white cloud appeared in the solution, due to the precipitation of water. The tube was again heated and the temperature at which the solution cleared was noted. The average of the temperatures for precipitation and the clearing of the solution was taken as the temperature of solubility. The data collected are reported in Table II and illustrated in the accompanying solubility curve (Fig. 2).

TABLE II

H_2O Gram	Chloropicrin		Temperature of Miscibility ° C.	H_2O per 100 G Chloropicrin
	Cc.	G.		
0.1098	29.3	48.49	55	0.2265
0.1098	35.8	59.25	50.8	0.1853
0.1098	40.3	66.70	48	0.1647
0.1098	53.4	88.38	41	0.1243
0.1098	56.0	92.68	36	0.1185
0.1098	66.0	109.25	32	0.1003

CONCLUSIONS

1—Chloropicrin is only slightly soluble in water, the solubility decreasing with increase in temperature.

2—Water is only slightly soluble in chloropicrin, the solubility increasing with increase in temperature.

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[1] This method was secured from the Bureau of Mines.

CONTROL EXPERIMENTS IN CHLOROPICRIN MANUFACTURE. I—THE EFFECT OF VARYING QUANTITIES OF LIME UPON THE YIELD OF CHLOROPICRIN[1]

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Received July 14, 1920

In the manufacture of chloropicrin at the Edgewood Arsenal during the summer of 1918, the method involved the following steps: The preparation of the soluble lime salt of picric acid by mixing picric acid and an excess of lime with water, the preparation of a sludge of water and bleaching powder, the mixing of these two solutions in the large reactors, and the digestion and steam distillation which gave chloropicrin in the distillate. The production of large quantities of chloropicrin by this method was realized, although the employment of the violently explosive picric acid necessitated the exercise of care and vigilance at all times. To avoid danger and to decrease expense, it was necessary to conduct the reaction in such a way as to produce the highest yield of the final product. The employment of calcium picrate instead of picric acid in the reaction was in harmony with the dictates of safety, since the lime salt is much more soluble than the free acid (or even the sodium salt), and the difficulties involved in working in dilute solutions or in nonhomogeneous suspensions were thereby completely avoided. It seemed the part of wisdom to prepare solutions in the presence of an excess of lime which served as a margin of safety in the operation of the process. The laboratory was requested to investigate the effect of adding varying quantities of lime upon the yields of chloropicrin.

EXPERIMENTAL METHOD

The materials employed for the preparation of chloropicrin were carefully analyzed, with the following results:

Lime	95.54 per cent CaO
Picric acid	99.80 per cent free acid, no sulfates
Bleaching powder	
Sample 1	33.30 per cent available chlorine
Sample 2	32.21 per cent available chlorine
Sample 3	33.3 per cent available chlorine

The best yields were obtained when the bleaching powder was made up to a thick paste with water, and the solution of picric acid or calcium picrate, as the case might be, was added in small portions with shaking and cooling, the temperature being kept below 30° C. The loss of chloropicrin was prevented by keeping the flask tightly stoppered during the addition. For a neutral solution 300 g. of bleaching powder, 30 g. of picric acid, and 3.85 g. of lime were employed.

Before conducting the steam distillation, the flask was connected to the condenser and gently heated until the yellow color had disappeared. Too rapid heating at this point not only led to lower yields of chloropicrin but also left a yellow residue, which was not decolorized upon subsequent treatment with bleaching powder, followed by steam distillation. From the distillate the chloropicrin lower layer was drawn off and weighed, the amount dissolved in the aqueous layer being estimated from the solubility curve. Ordinarily, the latter quantity increased the yield by about 1 per cent. Yields are reported on the basis of the ratio by weight of chloropicrin to picric acid.

To illustrate the importance of keeping the mixture cool during the picric acid or picrate addition, four experiments were conducted in which the picric acid was added in one step without cooling, the ratios obtained being 1.68, 1.68, 1.67, and 1.65. Upon repetition of the experiment with cooling and stepwise addition of the picric acid, the ratio was 1.75 in two experiments.

In all the experiments, 30 g. picric acid, 300 g. bleaching powder, and 1200 g. water were employed.

The yields obtained by varying the amount of lime are shown in the following table:

Amount of Lime	Wt. of Chloropicrin / Wt. of Picric Acid
0	1.76
	1.75
	1.75
3.85 g. (no excess)	1.76
	1.80
	1.73
	1.79
	1.75
	1.74
	1.78
4.24 g. (10 per cent excess)	1.72
	1.76
	1.78
	1.78
	1.79
	1.69
	1.71
	1.76
	1.77
	1.76
5.00 g. (30 per cent excess)	1.72
	1.69
	1.67
	1.78
	1.79
	1.82
	1.79
	1.78
	1.78

CONCLUSION

Under conditions which approximated as closely as possible those employed in the chloropicrin plant at Edgewood Arsenal, an excess of lime had no influence upon the yield of chloropicrin. Indirect support of this conclusion was furnished by some experiments conducted by Rowland J. Clark, at Edgewood, which showed that upon refluxing chloropicrin with water or calcium hydroxide very little hydrolysis occurs. After refluxing for one hour with water, it was found by estimating the chloride ion liberated, that 0.21 per cent of the chloropicrin was hydrolyzed. With calcium hydroxide solutions the hydrolysis which occurred in one hour was practically the same as with water, *viz.*, 0.24 per cent. The absence of nitrites in the residue from the refluxing with calcium hydroxide was established by a qualitative test. This fact is somewhat surprising, since at the boiling point of chloropicrin brown fumes are evolved, frequently with explosive violence.

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[1] Published by permission of the Chief of the Chemical Warfare Service.

CONTROL EXPERIMENTS IN CHLOROPICRIN MANUFACTURE. II—ACTIVE CHLORINE IN THE SLUDGE FROM THE MANUFACTURE OF CHLOROPICRIN[1]

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In the manufacture of chloropicrin it was necessary to use a fairly large excess of bleaching powder in order to decompose completely the calcium picrate during the steam distillation. It was obviously desirable to know what happened to this excess of bleaching powder during the steam distillation.

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[1] Published by permission of the Chief of the Chemical Warfare Service.

The following experiments establish the approximate rate at which active chlorine disappears during steam distillation, first, in the residue left after the preparation of chloropicrin, and, second, in a more concentrated solution containing the same concentration of bleaching powder as that originally present in the chloropicrin stills. Finally, analyses were made to determine the concentration of active chlorine remaining in each of the ten plant stills at the end of the distillation which removed the chloropicrin from the sludge.

Table I—Percentages of Active Chlorine

After Distilling off Chloropicrin	After 0.5 Hr. Steam Distillation	After 1.5 Hrs. Steam Distillation
0.0330	0.0262	0.0157
0.0505	0.0218	0.0172
0.0459	0.0242	0.0160

The residue left in the flask when chloropicrin was prepared as described in the preceding paper was analyzed for available chlorine by the iodometric method. The sludge was then subjected to steam distillation for periods of one-half and one and one-half hours, respectively. The analyses furnish approximate data for the rate at which bleaching powder is decomposed by steam.

When higher initial concentrations of the hypochlorite were employed, the rate of decomposition with steam was noticeably higher. The initial concentrations shown in Table II correspond to those employed in the plant.

Table II—Percentages of Active Chlorine

Initial	After 1 Hr. Steam Distillation	After 2 Hrs. Steam Distillation
6.98	2.52	0.714
6.18	3.21	0.747

Samples of the sludge left in the chloropicrin stills at the end of the distillation were analyzed. The conditions under which the various runs were made and the concentrations of the active chlorine based upon the weight of the sludge are shown in Table III. The results show that the concentration of active chlorine is very low in all cases.

Table III

No. of Still	Max. Temp. during Distillation	Percentage Active Cl in Sludge
1	102.0	0.28
2	103.5	0.24
3	104.0	0.28
4	105.0	0.28
5	100.0	0.285
6	104.0	0.32
7	104.0	0.29
8	105.0	0.29
9	101.0	0.26
10	104.0	0.22

ORIGINAL PAPERS

A STUDY OF THE REACTIONS OF COAL SULFUR IN THE COKING PROCESS[1,2]

By Alfred R. Powell

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PREVIOUS INVESTIGATIONS

The sulfur of coal has now been definitely established to exist as pyrite or marcasite, FeS_2, organic sulfur, and a rather small amount of sulfates, and accurate methods have been devised for the determination of these different forms.[3] The behavior of each form during the destructive distillation of coal is of theoretical interest, as well as of the greatest technical importance, since the reactions of the coal sulfur will determine the percentage of sulfur left in the coke and the nature and the amount of the sulfur compounds in the by-products.

The percentage of coal sulfur expelled during the coking process varies over wide limits, and this variation has always been supposed to be due to different relative percentages of sulfur forms in the coal.[4] M'Callum states[5] that he separated coal into different fractions by specific gravity methods, thereby securing a partial separation of the organic and the inorganic sulfur. From coking tests on these fractions he concluded that a somewhat greater percentage of the organic sulfur was volatilized than the inorganic, but no very sharply cut difference was noticeable. J. R. Campbell[1] stated that most of the coal sulfur was present as pyrite, that 42 per cent of this was volatilized during the coking process, and that the remainder was left in the coke as pyrrhotite. He also stated that most of the organic sulfur was retained in the coke.

Some tentative conclusions have been drawn by S. W. Parr[2] concerning sulfur in the coking process from his work on the low temperature carbonization of coal. He states that "the organic sulfur in the raw coal and half of the sulfur of FeS_2 is for the most part discharged at relatively low temperatures." This occurs at about 500° C. At about 700°, the sulfur of the FeS formed from the FeS_2 is taken up by carbon, leaving free iron in the coke.

It therefore appears that different investigators have obtained widely divergent results, and have advanced many different theories as to the reactions undergone by the coal sulfur during carbonization. The present investigation was undertaken with the idea of carbonizing a variety of coals under carefully controlled conditions, and studying the character and amount of the various sulfur compounds formed. Since these analyses were to be made over every period of the carbonization process, a complete and detailed picture could be obtained of the changes occurring in the coal sulfur.

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[1] Published by permission of the Director of the U. S. Bureau of Mines.

[2] Presented by title at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

[3] A. R. Powell and S. W. Parr, "A Study of the Forms in Which Sulfur Occurs in Coal," University of Illinois, Engineering Experiment Station, *Bulletin* **111** (1919).

[4] Fulton, "Treatise on Coke," International Textbook Co., Scranton, Pa., **1905**, pp. 38–40.

[5] *Chem. Eng.*, **11** (1910), 27.

[1] *Bull. Am. Inst. Mining Eng.*, **1916**, 177.

[2] *Ibid.*, **1919**, 1807.

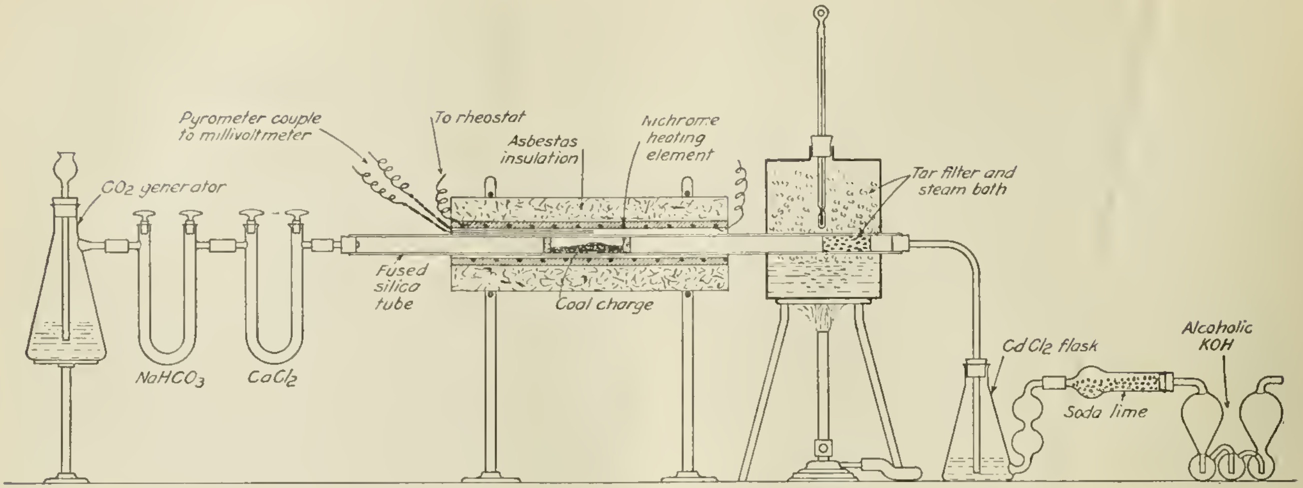

FIG. I—APPARATUS USED IN THE STUDY OF COAL SULFUR CONVERSION IN THE COKING PROCESS

APPARATUS

The apparatus was designed to coke about 5 g. of coal, and was so arranged that the temperature of the coking chamber could be controlled at all times to within a few degrees. At first thought, criticism might be made of this procedure, in that the quantity of coal used was so small. However, when it is considered that the primary coking reaction was desired, without the secondary effects produced by the travel of the gases through the hot coking mass, it is seen that the use of such a small quantity is essential. Furthermore, uniform temperature and close temperature control are impossible with a large quantity of coal.

Details of the coking apparatus as finally perfected are shown in Fig. 1. The coking chamber consisted of a five-eighths inch fused silica tube. The coking charge of 5 g. of the powdered coal was evenly distributed over 4 in. of the middle portion, with asbestos plugs at each end of the charge. A cotton plug was placed at the outlet end of the tube to act as a tar filter.

The charge was heated by a nichrome-wound tube furnace, which consisted of an alundum tube, of a somewhat greater diameter than the tube containing the charge, around which was wound nichrome wire of such a size and length that 1000° could be easily attained. The resistance wire was set in a mixture of alundum cement and water glass, and heat insulation was obtained by wrapping around the furnace several layers of heavy asbestos paper. Temperature readings were taken by means of a Hoskins thermocouple, the end of which rested against the outside of the coking tube at the point where the coal charge had been placed. Since the temperature of the run was maintained for 2 hrs. in the furnace, the temperature on the outside and inside of the silica tube must have been the same.

A slow stream of dry carbon dioxide was passed into the inlet end of the coking tube during certain periods of the run to act as a rinsing agent. This carbon dioxide was generated by the action of hydrochloric acid on calcium carbonate, and was passed through sodium bicarbonate and calcium chloride. This procedure was followed only at the beginning of a run to insure a non-oxidizing atmosphere over the coking charge, and at the end of the run to rinse out the last traces of volatile sulfur compounds.

The outlet and tar filter end of the tube was surrounded by a copper water bath of the design used by the Steel Corporation for the same purpose. By means of this device the temperature of the tar filter was at all times kept at 90°. The gas from the outlet end of the tube passed directly into a flask containing ammoniacal cadmium chloride which removed the hydrogen sulfide. The gas then passed through an absorption bulb containing absolute alcoholic potash, by means of which the presence of carbon bisulfide could be established. This last absorption bulb was replaced in certain runs by a Referee's total sulfur apparatus.

METHOD OF PROCEDURE

After the charge of coal had been placed in the tube and the steam bath around the tar filter brought up to the required temperature, a stream of carbon dioxide was started through the tube, and at the same time the heating current was turned on. After a few minutes the carbon dioxide was shut off, and the electric current was carefully regulated by means of a rheostat so as to bring the temperature slowly up to that required for the run. In the case of the higher temperature runs this gradual increase sometimes required as much as one hour.

SULFUR IN TAR—The run was continued for 2 hrs. at the temperature desired, this length of time being considered necessary to bring the reactions to equilibrium. The current was then shut off and carbon dioxide again run through for a few minutes. The coking tube was removed from the furnace, and as much of the tar as possible taken out for a sulfur analysis, which was made by the use of Eschka mixture. This determination must be considered only approximate, but, since it involved such a small portion of the coal sulfur, was sufficiently accurate for this investigation.

SULFUR IN COKE—The coke was shoved out of the tube by means of a long iron rod, separated as thoroughly as possible from the asbestos plugs, and ground

TABLE I—SOURCE AND PROXIMATE ANALYSIS OF COALS USED IN EXPERIMENTS

No.	Name	Source	Moisture	Volatile Matter	Fixed Carbon	Ash	Sulfur
21100	Tennessee	Tennessee, Morgan Co. Coal Creek, Couger-Baker	0.74	39.05	52.40	7.80	4.25
20507	Pocahontas	West Virginia, McDowell Co , Pocahontas No. 3, Mine No. 7	0.39	22.88	70.47	6.25	0.56
18847	Pittsburgh	Pennsylvania, Bruceton, Experimental Mine, Bureau of Mines	1.57	38.72	54.95	4.75	1.72
23066	Upper Freeport	Pennsylvania, Butler Co., Upper Freeport, Cunningham Coal Co	2.04	33.11	56.36	8.49	1.21
33945	Joliet	Mixture of 65% Pocahontas, 20% Lynch, Ky., and 15% washed Franklin Co., Ill., coal. As charged at coke ovens, Illinois Steel Co., Joliet	0.92	26.28	65.60	7.20	0.82
33819	Raw Vandalia	Vandalia, Ind.	2.35	38.05	49.60	10.00	1.38
33820	Washed Vandalia	Vandalia, Ind. Same as above but washed	2.48	39.52	50.73	7.27	1.18

[1] All samples were in an air-dry condition.

in a porcelain mortar to 100-mesh size. It was then placed in a flask so arranged that a current of hydrogen could be passed through and the outgoing gas bubbled through ammoniacal cadmium chloride. One hundred cc. of a 1 : 1 mixture of concentrated hydrochloric acid and water were poured over the coke and the contents of the flask heated to boiling, for about 15 min., while a brisk stream of hydrogen was passed through. The hydrogen sulfide given off was a measure of the metallic sulfide content of the coke, that is, the ferrous sulfide and pyrrhotite. It was estimated by treating the cadmium sulfide precipitate with an excess of hydrochloric acid and standard iodine solution, and titrating back with thiosulfate.

A sulfur analysis of the hydrochloric acid extract filtered off from the coke gave the sulfate content of the coke. The coke was then treated with 1 : 3 mixture of concentrated nitric acid and water, and allowed to stand at room temperature for 24 hrs. The extract was filtered, the nitric acid evaporated off, and sulfur and iron determined in the resulting residue. By this means the undecomposed pyrite of the coke was figured. The iron value proved to be a good means of checking the sulfur, since the iron-sulfur ratio proved whether or not the nitric acid had selectively extracted pyrite.

In most cases the residual coke was discarded, the sulfur in it being calculated by difference, but in a few runs the sulfur was determined directly. In all such cases the sum of the sulfur determinations checked very closely with the total sulfur of the coal.

SULFUR IN VOLATILE MATTER—The sulfur which had been given off from the coal in the form of hydrogen sulfide had been caught in the ammoniacal cadmium chloride flask of the coking apparatus. It was estimated as just described under the determination of metallic sulfide in the coke. Carbon bisulfide in the volatile matter was tested for by boiling the contents of the alcoholic potash absorption bulb, acidifying with acetic acid, and adding copper acetate. The presence of a reddish brown precipitate would indicate carbon bisulfide.

DESCRIPTION OF COALS USED

Eight coals were used during these investigations. Table I gives the laboratory number, the name under which the coal will be referred to hereafter, a general description of the source, and the proximate analysis of each coal.

TABLE II—ANALYSIS OF SULFUR FORMS
(Values given in per cent, air-dry basis)

No.	Coal	Total	Pyritic	Sulfate	Organic
21100	Tennessee	4.25	1.75	0.71	1.79
20507	Pocahobtas	0.56	0.08	0.01	0.47
18847	Pittsburgh	1.72	0.79	0.23	0.70
23066	Upper Freeport	1.21	0.47	0.07	0.67
33945	Joliet	0.82	0.26	0.00	0.56
33819	Raw Vandalia	1.38	0.70	0.03	0.65
33820	Washed Vandalia	1.18	0.25	0.03	0.90

A complete analysis, by the method of Powell and Parr,[1] was made on all the coals for the different forms of sulfur present. The results are given in Table II.

EXPERIMENTAL RESULTS

EFFECT OF TEMPERATURE ON PYRITE—Since pyrite is one of the most important sulfur constituents of coal, it was necessary to study its behavior at different temperatures before going ahead with the study of coal itself. Very little pyrite was decomposed up to 500°, but at 1000° the decomposition was complete. Table III shows the changes in the forms of sulfur in mineralogical pyrite between 0° and 1000°.

TABLE III—ANALYSIS OF PYRITE BEFORE AND AFTER DECOMPOSITION AT 1000° C.

	0° C.	1000° C.
Pyritic Sulfur	48.52	0.00
Sulfate Sulfur	0.16	0.00
Free Sulfur	0.00	21.88
Sulfide Sulfur	0.00	24.24
Sulfur as H_2S	0.00	2.56
TOTAL	48.68	48.68

These results point pretty clearly to the following reaction:

$$FeS_2 = FeS + S$$

The sulfide content of the decomposed pyrite is practically in quantitative accordance with this reaction. Owing to the presence of moisture or other hydrogen yielding bodies, a small part of the free sulfur has been converted into hydrogen sulfide.

After pyrite has been heated the residue is almost invariably magnetic. This is not due to the presence of free iron but to the fact that the residue is not plain ferrous sulfide, but pyrrhotite, or magnetic sulfide of iron. It has been shown that pyrrhotite is not a definite compound, but is a solid solution of sulfur in ferrous sulfide.[2] The amount of sulfur which is present in the sulfide is determined by the temperature and the partial pressure of free sulfur over it. In an atmosphere of hydrogen sulfide, the maximum amount of sulfur retained in ferrous sulfide is 6.0 per cent at 600°. At 1000° the percentage is 3.5 per cent, and at 1300° it is 2.0 per cent.

At 1000° the partial pressure of free sulfur in an atmosphere of hydrogen sulfide is 70 mm., or a little less than one-tenth of an atmosphere. This amount of free sulfur in the space above the pyrrhotite holds its content of dissolved sulfur at 3.5 per cent, as has been stated. If, however, as is true in actual practice, the amount of hydrogen sulfide, and therefore the amount of free sulfur, present is very small, the percentage of sulfur dissolved in the ferrous sulfide is very much less than 3.5 per cent. When the residue from the heated pyrite was dissolved in acid, the sulfur left undissolved and in the free state was denoted by a very slight cloudiness of the solution. The indications were that it would amount to only a very small fraction of one per cent. Under these circumstances, it can be neglected for quantitative purposes, although it explains the weakly magnetic character of the pyrite residue.

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[1] *Loc. cit.*

[2] E. T. Allen, J. L. Crenshaw and John Johnston, "The Mineral Sulfides of Iron," *Am. J. Sci.*, **33** (1912), 169.

Because of these considerations, all the calculations of this investigation have been based on the decomposition of pyrite to form ferrous sulfide and free sulfur, but it must be remembered that a small part of the sulfur remains in the ferrous sulfide in the form of a solid solution.

No free iron existed in the residue from decomposed pyrite or in finished coke, as shown by microscopic tests. When an acid solution of a copper salt was added to the finely powdered substance no metallic copper could be detected under the microscope, thus proving the absence of free iron.

DECOMPOSITION OF PYRITE-COAL MIXTURE—A further study of the decomposition products of pyrite was made, in which the pyrite was incorporated with a coal of known composition, so that all secondary reactions could be noted. The mixture contained 50 per cent of mineralogical pyrite and 50 per cent of Tennessee coal. The results of this test are given in Table IV.

TABLE IV—DECOMPOSITION OF PYRITE-COAL MIXTURE AT 1000° C.

	0°	1000°
Pyritic Sulfur	25.14	0.00
Sulfate Sulfur	0.39	0.00
Organic Sulfur	0.90	1.93
Free Sulfur	0.00	5.22
Sulfide Sulfur	0.00	13.12
Sulfur as H_2S	0.00	6.08
Tar Sulfur	0.00	0.08
TOTAL	26.43	26.43

It may safely be assumed that the sulfate form will be reduced to the sulfide. Subtracting the sulfide sulfur from this source from the total sulfide sulfur leaves 12.73 per cent as the sulfide sulfur coming from the pyrite. This figure is very close to 12.57 per cent or one-half the pyrite sulfur. The complete decomposition of pyrite in coal must therefore yield ferrous sulfide and free sulfur, which later changes to hydrogen sulfide if an excess of hydrogen yielding matter is present.

TENNESSEE COAL—The results of a complete study made upon the Tennessee coal of sulfur distribution at different temperatures are given in Table V.

It will be noted that the sulfur not found in any other type of compound is placed under the head of "organic sulfur." That the coal sulfur other than that of the pyrite and sulfates is organic in nature has been proved.[1] This organic sulfur persists almost unchanged in type up to 400°. Between 400° and 500° a decided change in its characteristics takes place. This is shown by the fact that treatment with nitric acid and subsequent treatment with ammonia does not take into solution the compounds containing the organic sulfur.

That organic sulfur is present, even in the finished coke, and that its percentage is higher in the coke than it was in the original coal has been well proved by Wibaut and Stoffel,[2] who have produced a form of organic sulfur much resembling that of the coke by heating together sulfur and sugar.

From the results given in Table V, it is possible to calculate the nature and magnitude of the probable reactions undergone by the various forms of coal sulfur during the coking process. This is simplified by the preliminary study of pyrite decomposition. In the presence of a large excess of coal substance, pyrite decomposes quantitatively into ferrous sulfide and hydrogen sulfide. Also it may safely be assumed that any sulfate present will be reduced to sulfide. The pyrite decomposed will give a measure of the hydrogen sulfide from this source, but in every case the actual hydrogen sulfide produced is greater than this. A probable source of this excess hydrogen sulfide is the organic sulfur, which makes a third probable reaction. The sulfur of the tar, being entirely of an organic nature, must find its origin in the organic sulfur of the coal. This makes a fourth measurable reaction. It may be noticed that the sulfide sulfur of the coke is generally present in smaller amount than would be formed from the decomposition of the pyrite and the reduction of the sulfate form. This seems to be accounted for by a rather peculiar reaction, namely, the transference of a portion of the sulfur combined as sulfide to a sulfur-carbon combination. This fifth reaction has been noted by other investigators.[1] The evidence for this last reaction is simply the fact that during the latter stages of the coking process there is quite a decided increase in the sulfur held in the carbon-sulfur combination, with a decrease in the amount of sulfides present. The carbon-sulfur combination formed by this reaction has all the properties of the remainder of the sulfur existing in this form in the coke.

TABLE V—DISTRIBUTION OF SULFUR IN TENNESSEE COAL NO. 21100
(Values given in percentage by weight of original air-dried coal)

	0°	300°	400°	500°	600°	1000°
Pyritic Sulfur	1.75	1.75	1.42	0.31	0.00	0.00
Sulfate Sulfur	0.71	0.55	0.44	0.01	0.01	0.00
Organic Sulfur	1.79	1.63	1.51	1.70	1.87	1.81
Sulfide Sulfur	0.00	0.13	0.44	0.93	0.82	0.84
Sulfur as H_2S	0.00	0.19	0.39	1.20	1.39	1.44
Tar Sulfur	0.00	0.00	0.05	0.10	0.16	0.16
Sulfur as CS_2	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL	4.25	4.25	4.25	4.25	4.25	4.25

TABLE VI—REACTIONS OCCURRING IN CARBONIZATION OF TENNESSEE COAL (Results expressed in per cent sulfur on basis of air-dried coal)

Temperature Range ° C.	$FeS_2 = FeS + H_2S$	$MSO_4 = MS$	Organic S = H_2S	Organic S = Tar S	MS = Organic S
0–300	0.00	0.16	0.19	0.00	0.00
300–400	0.33	0.11	0.05	0.05	0.00
400–500	1.11	0.43	0.25	0.05	0.49
500–600	0.31	0.00	0.03	0.06	0.26
600–1000	0.00	0.01	0.05	0.00	—0.02
TOTAL	1.75	0.71	0.57	0.16	0.73

In addition to the five reactions or classes of reactions enumerated above, there are several others which have been noted but have not been measured, owing either to their complexity or to difficulties of analysis. Prominent among these is the formation of pyrrhotite, already noted, and the decided transformation in the characteristics of the organic sulfur compounds between 400° and 500°. Other reactions, of a secondary nature, also occur in retorts. Reactions between the organic sulfur compounds and hydrogen of the gas to form hydrogen sulfide, and between

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[1] Powell and Parr, *Loc. cit.*

[2] *Rec. trav. chim.*, **38** (1919), 132.

[1] S. W. Parr, *Am. Inst. Mining Eng.*, **1919**, 1807; J. P. Wibaut and A. Stoffel, *Loc. cit.*

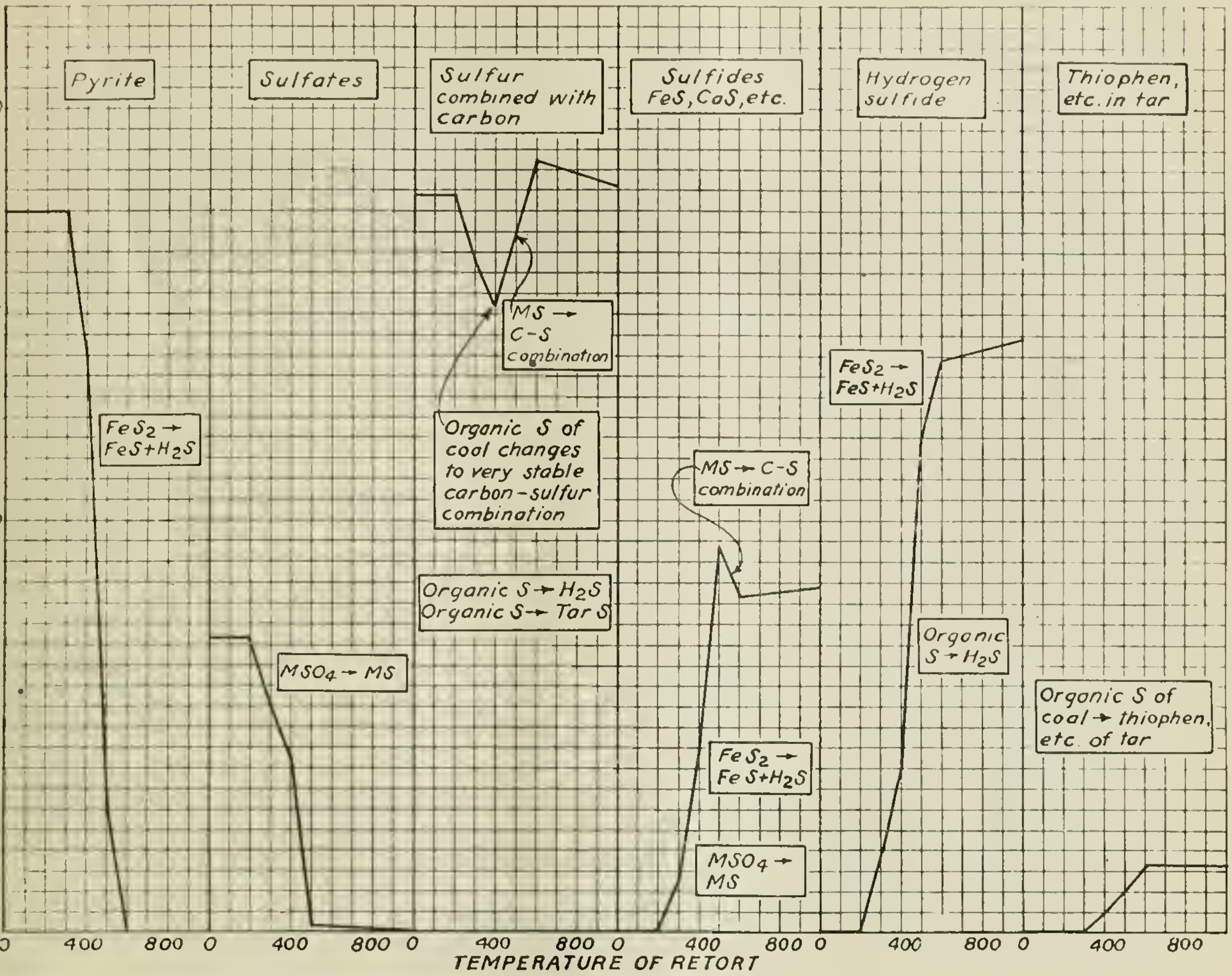

Fig. 2—Series of Curves Showing Variations of Sulfur Constituents at Successive Temperatures of Distillation of Tennessee Coal, No. 21100. Reactions Causing the Variations Are Noted

hydrogen sulfide and red-hot coke to form carbon bisulfide may be mentioned as typical. That carbon bisulfide is not a primary product of coal distillation is shown by the results obtained above. This fact has been known for some time.[1]

Following the facts given above, the magnitude of each of the five measurable reactions has been calculated for each temperature range. A summary of these calculations is given in Table VI, the results being expressed in the per cent of sulfur undergoing the reaction on the basis of the original air-dried coal. It was necessary to express results in this manner in order to get comparable figures.

The courses of these reactions are represented graphically in Fig. 2. The decomposition of the pyrite begins at 300°, is complete at 600°, and reaches its maximum between 400° and 500°. The reduction of the sulfates is practically complete at 500°. From one-quarter to one-third of the organic sulfur is decomposed with the production of H_2S, this decomposition occurring for the most part below 500°. At the lower temperatures of coking, a small part of the organic sulfur finds its way into the tar. Not more than one-tenth of the coal organic sulfur is so distributed. From 400° to 500° a large part of the ferrous sulfide is decomposed, the sulfur apparently entering into combination with the carbon.

POCAHONTAS COAL—The values for sulfur distribution in the Pocahontas coal are given in Table VII, and a summary of its reactions in Table VIII.

Table VII—Distribution of Sulfur in Pocahontas Coal, No. 20507
(Values given in per cent of original air-dried coal)

	0°	300°	400°	500°	600°	1000°
Pyritic Sulfur	0.08	0.07	0.09	0.01	0.00	0.00
Sulfate Sulfur	0.01	0.02	0.02	0.00	0.00	0.00
Organic Sulfur	0.47	0.47	0.44	0.43	0.35	0.27
Sulfide Sulfur	0.00	0.00	0.00	0.04	0.05	0.09
Sulfur as H_2S	0.00	0.00	0.01	0.06	0.13	0.17
Tar Sulfur	0.00	0.00	0.00	0.02	0.03	0.03
Sulfur as CS_2	0.00	0.00	0.00	0.00	0.00	0.00
Total	0.56	0.56	0.56	0.56	0.56	0.56

Table VIII—Reactions Occurring in Carbonization of Pocahontas Coal (Results expressed in per cent sulfur on basis of air-dry coal)

Temperature Range, ° C.	FeS_2 = FeS + H_2S	MSO_4 = MS	Organic S = H_2S	Organic S = Tar S	MS = Organic S
0–300	0.00	0.00	0.00	0.00	0.00
300–400	0.00	0.00	0.01	0.00	0.00
400–500	0.07	0.01	0.01	0.02	0.00
500–600	0.01	0.00	0.07	0.01	—0.01
600–1000	0.00	0.00	0.04	0.00	—0.04
Total	0.08	0.01	0.13	0.03	—0.05

This coal differs from the Tennessee coal in that it is of a semi-bituminous type and also in the fact that its sulfur content is considerably lower. Furthermore, a very large proportion of the total sulfur is organic, with very little pyrite and practically no sulfate. This may account for some of the differences in the reactions between the two coals.

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[1] Lewes, "The Carbonization of Coal," John Allan & Co., **1912**, p. 274.

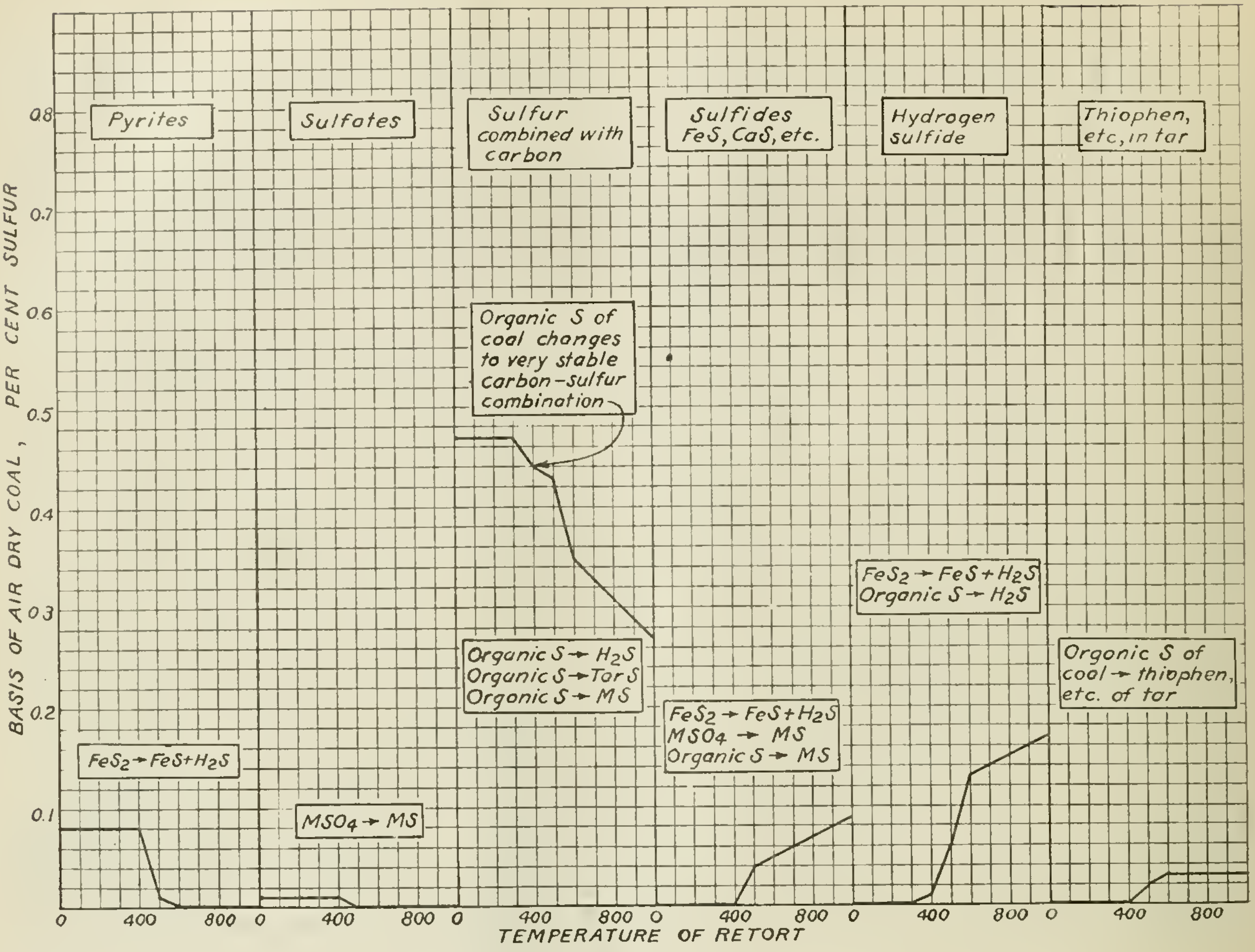

Fig. 3—Series of Curves Showing Variations of Sulfur Constituents at Successive Temperatures of Distillation of Pocahontas Coal, No. 20507. Reactions Causing the Variations Are Noted

The reactions of the sulfur in the Pocahontas coal are shown graphically in Fig. 3. In two particulars, these reactions differ materially from those of the Tennessee coal. The decomposition of the organic sulfur to form hydrogen sulfide is more pronounced at the higher temperatures than at the lower degrees of heat. Instead of a tendency of the sulfide sulfur to be converted into organic sulfur, the reverse of this seems to be true above 500°. This can be explained by the fact that very little sulfide sulfur can be formed from the small percentage of pyrite and sulfate, whereas organic sulfur is present in fairly large quantities. The reaction would seem to be reversible and an excess of one form of sulfur causes the equilibrium to shift toward the other form.

PITTSBURGH COAL—In Tables IX and X are given the results obtained for the Pittsburgh coal. This was carbonized at only two temperatures, 500° and 1000°.

Table IX—Distribution of Sulfur in Pittsburgh Coal, No. 18847
(Value given in per cent of original air-dried coal)

	0°	500°	1000°
Pyritic Sulfur	0.79	0.32	0.00
Sulfate Sulfur	0.23	0.00	0.00
Organic Sulfur	0.70	0.74	0.98
Sulfide Sulfur	0.00	0.23	0.16
Sulfur as H_2S	0.00	0.38	0.53
Tar Sulfur	0.00	0.05	0.05
Sulfur as CS_2	0.00	0.00	0.00
Total	1.72	1.72	1.72

Table X—Reactions Occurring in Carbonization of Pittsburgh Coal (Results expressed in per cent sulfur on basis of air-dried coal)

Temperature Range ° C.	FeS_2 = FeS + H_2S	MSO_4 = MS	Organic S = H_2S	Organic S = Tar	MS = Organic S
0–500	0.47	0.23	0.15	0.05	0.24
500–1000	0.32	0.00	0.00	0.00	0.23
Total	0.79	0.23	0.15	0.05	0.47

A study of these reactions reveals the fact that they do not differ essentially from those undergone by the Tennessee coal.

UPPER FREEPORT COAL—The Upper Freeport coal gave the results and reactions shown in Tables XI and XII.

Table XI—Distribution of Sulfur in Upper Freeport Coal, No. 23066
(Values given in per cent of original air-dried coal)

	0°	500°	1000°
Pyritic Sulfur	0.47	0.33	0.00
Sulfate Sulfur	0.07	0.01	0.00
Organic Sulfur	0.67	0.58	0.66
Sulfide Sulfur	0.00	0.09	0.12
Sulfur as H_2S	0.00	0.17	0.40
Tar Sulfur	0.00	0.03	0.03
Sulfur as CS_2	0.00	0.00	0.00
Total	1.21	1.21	1.21

Table XII—Reactions Occurring in Carbonization of Upper Freeport Coal (Results expressed in per cent sulfur on basis of air-dried coal)

Temperature Range ° C.	FeS_2 = FeS + H_2S	MSO_4 = MS	Organic S = H_2S	Organic S = Tar S	MS = Organic S
0–50'	0.14	0.06	0.10	0.03	0.04
500–1000	0.33	0.01	0.06	0.00	0.14
Total	0.47	0.07	0.16	0.03	0.18

In general, these reactions resemble those of the coals already described.

JOLIET COAL—Through the courtesy of Mr. J. V. Freeman, chief chemist of the central laboratory of the Illinois Steel Co., a sample of the coal as it is charged into the by-product ovens at that plant was obtained. A sample of the coke from the ovens was also obtained for comparison. This comparison is given later in the paper. The results obtained on this by-product coking coal are given in Tables XIII and XIV.

TABLE XIII—DISTRIBUTION OF SULFUR IN JOLIET COAL, No. 33945
(Values given in per cent of original air-dried coal)

	0°	500°	1000°
Pyritic Sulfur	0.26	0.12	0.00
Sulfate Sulfur	0.00	0.00	0.00
Organic Sulfur	0.56	0.44	0.49
Sulfide Sulfur	0.00	0.08	0.06
Sulfur as H_2S	0.00	0.16	0.25
Tar Sulfur	0.00	0.02	0.02
Sulfur as CS_2	0.00	0.00	0.00
TOTAL	0.82	0.82	0.82

TABLE XIV—REACTIONS OCCURRING IN CARBONIZATION OF JOLIET COAL
(Results expressed in per cent sulfur on basis of air-dried coal)

Temperature Range ° C.	$FeS_2 = FeS + H_2S$	$MSO_4 = MS$	Organic S $= H_2S$	Organic S = Tar S	MS = Organic S
0–500	0.14	0.00	0.09	0.02	0.00
500–1000	0.12	0.00	0.03	0.00	0.07
TOTAL	0.26	0.00	0.12	0.02	0.07

The general course of reactions in this mixed coking coal resembles that of the majority of coals studied.

RAW AND WASHED VANDALIA COAL—Comparative tests were made between a coal in the raw state and the same coal after passing through a washery. The results of these tests are given in Tables XV and XVI.

TABLE XV—DISTRIBUTION OF SULFUR IN RAW VANDALIA COAL, No. 33819, AND WASHED VANDALIA COAL, No. 33821 (Values given in per cent of original air-dried coal)

	Raw			Washed		
	0°	500°	1000°	0°	500°	1000°
Pyritic Sulfur	0.70	0.32	0.00	0.25	0.12	0.00
Sulfate Sulfur	0.03	0.00	0.00	0.03	0.00	0.00
Organic Sulfur	0.65	0.50	0.70	0.90	0.63	0.66
Sulfide Sulfur	0.00	0.12	0.11	0.00	0.04	0.03
Sulfur as H_2S	0.00	0.41	0.54	0.00	0.36	0.46
Tar S	0.00	0.03	0.03	0.00	0.03	0.03
Sulfur as CS_2	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL	1.38	1.38	1.38	1.18	1.18	1.18

TABLE XVI—REACTIONS OCCURRING IN CARBONIZATION OF VANDALIA COALS (Results expressed in per cent sulfur on basis of air-dried coal)

COAL	Temperature Range ° C.	$FeS_2 = FeS + H_2S$	$MSO_4 = MS$	Organic S $= H_2S$	Organic S = Tar S	MS = Organic
Raw	0–500	0.38	0.03	0.22	0.03	0.10
Raw	500–1000	0.32	0.00	—0.03	0.00	0.17
TOTAL		0.70	0.03	0.19	0.03	0.27
Washed	0–500	0.13	0.03	0.29	0.03	0.05
Washed	500–1000	0.12	0.00	0.04	0.00	0.07
TOTAL		0.25	0.03	0.33	0.03	0.12

Some rather interesting comparisons can be made from these coals. In the raw coal, where the inorganic sulfur predominates, a larger quantity of metallic sulfides are converted into the organic form than in the washed coal. In the washed coal, where the organic sulfur predominates, more of the organic sulfur is decomposed into hydrogen sulfide than in the raw coal. Therefore, as might be expected, the extent to which a sulfur reaction will proceed depends very largely on the amount of the reacting constituent present.

The results obtained from the tests on these various coals check up very closely the conclusions arrived at from the series of tests on the Tennessee coal. One very noticeable exception was the Pocahontas coal in which organic sulfur was present in relatively very small quantity. Because of this there was no conversion of metallic sulfides into organic sulfur, but the reaction seemed to be the reverse of this. Exceptions of this kind may be expected where the sulfur constituents are in abnormal relation to each other.

DISTRIBUTION OF COAL SULFUR IN THE COKING PROCESS

A question which has long been of great interest to the coal and coke chemists of the country is that of the behavior of the different forms of coal sulfur during the coking process. Which is eliminated in the volatile matter in the greatest proportion—the organic sulfur or the pyritic sulfur? What conditions, if any, affect the distribution ratio of the two forms between the coke and the volatile products? The conclusions of previous investigators have varied widely on this point. Campbell believes that most of the organic sulfur remains in the coke. Parr, on the other hand, states that the organic sulfur is discharged for the most part at relatively low temperatures. M'Callum concludes that a somewhat greater percentage of the organic sulfur than of the inorganic was volatilized.

From the standpoint of coal washing, the question is an important one, since this process selectively removes the pyrite without touching the organic sulfur. If organic sulfur is volatilized in greater proportion than the pyritic sulfur, coal washing for coking coals is more efficient than the sulfur reduction in the coal would indicate. The facts are that washery men have always evaluated their practice by the sulfur and ash reduction secured, without any attention to the forms of sulfur removed. Table XVII is designed to bring out the data concerning the relation of the sulfur in the coal to that in the coke.

TABLE XVII—RELATION OF THE SULFUR FORMS OF THE COAL TO SULFUR IN THE COKE (Data based on sulfate-free coal, containing only organic and pyritic sulfur forms)

COAL	Organic Sulfur Per cent of Total S	Inorganic Sulfur Per cent of Total S	Sulfur in Coal Per cent	Sulfur in Coke Per cent	Sulfur in By-product Oven Coke Per cent
Pocahontas	85.5	14.5	0.55	0.45	....
Washed Vandalia	78.2	21.8	1.15	1.14	....
Joliet Coking	68.3	31.7	0.82	0.75	0.64
Upper Freeport	58.8	41.2	1.14	1.09	....
Tennessee	50.6	49.4	3.54	3.22	....
Raw Vandalia	48.1	51.9	1.35	1.30	....
Pittsburgh	47.0	53.0	1.49	1.51	....

It will be noted that all the data above have been calculated on the basis of sulfate-free coal. This is necessary since it is known that the sulfate form is completely retained in the coke and its presence in the calculations would obscure the essential data regarding the pyrite and organic sulfur. In freshly mined coal sulfates are normally absent.

The coals have been arranged in the table in the order of their relative content of organic sulfur, beginning with the highest proportion of organic sulfur. A careful scrutiny of the percentages of sulfur in the coals and the percentages of sulfur in the corresponding cokes will not reveal any constant difference. Furthermore, the differences between the two percentages do not vary as the proportion of organic sulfur, but seem to be entirely independent of this. These figures would seem to indicate that the total sulfur of the coal is the most important factor affecting the sulfur content of the coke, that the relative amount of sulfur forms present do not affect it materially, and that certain other factors, particularly the nature of the coal, will vary the amount of sulfur in the coke to a limited extent. That another factor, not considered up to this time, materially affects the sulfur content of coke will be shown later.

A comparison between the raw and the washed Vandalia coals shows that the sulfur reduction in the coke is not even as good as the corresponding reduction of sulfur in the coal. For all practical purposes, however, the sulfur in the two cokes is roughly proportional to the sulfur in the two coals, which strongly bears out the statement just made, namely, that the total sulfur of the coal is the main determining factor and not the relative quantity of organic and inorganic sulfur.

At the time the coking coal was obtained from the Joliet by-product plant, a sample of coke, made from this coal in the ovens, was also furnished. The sulfur analysis of this coke is given in the last column of the table. The reason for the difference in the sulfur content of the coke made in the laboratory and that made in the by-product ovens is found in a very interesting secondary coking reaction, which has been well proved, and will be described in a later paper. This reaction is one between the hydrogen of the by-product gases and the red-hot coke, which results in the formation of hydrogen sulfide and its ultimate removal from the oven. This decrease in the coke sulfur due to this secondary oven reaction would apply to all the cokes in the above table, but this increased difference between the percentage of sulfur in the coal and that of the coke would in no wise affect the conclusions reached as to the effect of the relative quantities of sulfur forms present. The comparison of these tests with actual operation is interesting, however, as showing the difference between the effect of the primary sulfur reactions, as worked out in the laboratory, and the combined effect of primary and secondary reactions as shown in the by-product coke oven.

The nature of the sulfur compounds in coke has always been a problem difficult to solve. The present investigation has brought out very little additional information on this subject. It still seems probable that the majority of the coke sulfur is organic, with a smaller quantity of iron sulfide present. The nature of this iron sulfide in coke has already been described.

Proof that a magnetic sulfide of iron existed in coke was established by the following experiment: Coke, made in the laboratory from the Joliet coking coal, was pulverized in a porcelain mortar. It was found that about one per cent of this coke could be separated from the remainder by means of a large horseshoe magnet. The magnetic portion contained 2.4 per cent, and the nonmagnetic portion 0.12 per cent of sulfide sulfur.

In other words, the magnetic portion contained twenty times the percentage of sulfide sulfur that was in the remainder. This would point to the presence in the coke of magnetic sulfide of iron or pyrrhotite. Campbell has previously indicated the presence of this substance in coke and this investigation confirms his statements, but exception is taken to his claim that pyrrhotite has the formula Fe_7S_8, the true nature of this substance having been indicated earlier in this paper. Free iron has not been detected in coke prepared under careful conditions, but has been found in large quantities in coke which has been ground in an iron or steel crusher, due solely to the erosion of the machinery.

CONCLUSIONS

Previous work has indicated that sulfur exists in coal in three typical forms—pyrite or marcasite, sulfates, and organic sulfur. A study of the changes which these forms undergo during coking has been made on a variety of coals, and the five following classes of reactions established:

1—Complete decomposition of the pyrite and marcasite to ferrous sulfide, pyrrhotite, and hydrogen sulfide. This reaction begins at 300° C., is complete at 600° C., and generally reaches its maximum between 400° and 500° C.

2—Reduction of sulfates to sulfides. This reaction is complete at 500° C.

3—Decomposition of the organic sulfur to form hydrogen sulfide. From one-quarter to one-third of the organic sulfur is so affected in the primary decomposition, but the by-product gases traveling through the coking mass increase this reaction to as much as one-half of the organic sulfur present. Primary decomposition is most active below 500° C.

4—Decomposition of a small part of the organic sulfur to form volatile organic sulfur compounds. The greater portion of these find their way into the tar. This decomposition occurs at the lower temperatures of the coking process.

5—Disappearance of a portion of the ferrous sulfide and pyrrhotite, the sulfur apparently entering into combination with the carbon. This reaction seems to be most active in the neighborhood of 500° and higher.

The organic sulfur not accounted for by the above reactions undergoes a decided change in character between 400° and 500° and shows none of the properties of the original coal sulfur.

This investigation indicates that the total sulfur of the coal is the most important factor affecting the sulfur content of the coke, that the relative amounts of sulfur forms present do not affect it materially, and that certain other factors, particularly the nature of the coal, will vary the amount of sulfur in the coke to a limited extent.

The secondary reaction between the sulfur of the red-hot coke and the hydrogen of the by-product gases traveling through it causes a more marked reduction in the amount of sulfur left in the coke than the above primary reactions would indicate.

A magnetic sulfide of iron, probably pyrrhotite, has been proved to be present in coke.

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THE DESULFURIZING ACTION OF HYDROGEN ON COKE[1,2]

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Sulfur has always been an objectionable constituent of coke, and, as the supply of low sulfur coal becomes less, the presence of more and more sulfur in metallurgical coke is a real problem. Coal washing has been resorted to in many regions where high sulfur coal is mined, but even efficient methods of washing often will not solve the problems, since this treatment removes a part of the sulfur which is combined as pyrites, but does not affect the finely disseminated iron pyrite or the sulfur in organic combination.[3] In most cases, one-fourth to one-half of the sulfur in coal can be removed by washing, which means a corresponding reduction in the coke sulfur, as has been shown previously by the author.[4]

PROCESSES FOR THE DESULFURIZATION OF THE COKE

In addition to methods for removing a portion of the sulfur in coal by washing, many schemes have been proposed for the removal of sulfur from the coke itself. All of these processes involve either the elimination of the sulfur as volatile compounds or its conversion into compounds which may later be leached out with water, and which, by their nature, are harmless for the uses to which the coke is to be put. A general summary of desulfurizing processes which have been patented or proposed follows.

PROCESSES INVOLVING THE PASSAGE OF GASES THROUGH THE COKING MASS. *Steam*—Scheerer[5] in 1854 passed high pressure steam into an oven before drawing the coke, and claimed a resultant loss of 0.4 per cent sulfur in the coke. A steam desulfurizing process was patented by Claridge and Roper in 1858. Woltereck[6] has a process combining the use of air and steam at not over 400° C., by which it is claimed the sulfur is driven out as the dioxide. The disadvantage of steaming processes is that an excessive amount of the coke is used up to secure desulfurization.

Air—The passage of air through red-hot coke was investigated by Philippart.[7] Elimination of a part of the sulfur as sulfur dioxide was secured, but only at the expense of a prohibitive portion of the coke. The use of air under high pressure with the coke at 300° C. did not give very efficient desulfurization.

Chlorine—Stoner[8] has a process in which coke is treated at the close of the coking operation with chlorine or chlorinated gases, and then washed to remove the soluble salts. This process is rather expensive, and furthermore tends to destroy the coke and by-products. Fingerland[1] passes chlorine through the hot coke after adding certain catalyzers, and claims that the sulfur passes off as sulfur dichloride.

Carbon monoxide—Several patents call for the use of carbon monoxide, but no data as to their efficiency are available.

PROCESSES INVOLVING THE ADDITION OF COMPOUNDS TO THE COAL BEFORE COKING—*Salt*—In England the Calvert process[2] made use of sodium chloride added to the coal before coking. The purpose was to form volatile compounds of sulfur and phosphorus with the chlorine of the salt, but later experiments have demonstrated that sulfur is actually increased in the coke by the addition of salt. The Rowan process, patented in 1868, made use of the addition of salt, with subsequent washing of the coke by immersion in water. It is claimed that this process gave good results, but it has never been applied on a commercial scale.

Sodium carbonate—This process, patented by Spurrier,[3] is not in reality a desulfurizing process, but is simply the addition of sodium carbonate in excess, to prevent the sulfur of the coke from uniting with the iron in the smelting operation.

Manganese dioxide—The addition of manganese dioxide to coal before coking has been patented by Franck.[4] The claim is made that the oxygen liberated effects a rapid combustion of the organic sulfur compounds, which are then removed with the gases. No mention is made of the simultaneous oxidation of the coal substance proper, which must be excessive.

PROPOSED METHOD

None of the coke desulfurization processes just described have ever found extensive application, and the author knows of no large-scale operation based on any of these processes in this country. Coke desulfurization must of necessity be cheap, must remove a large percentage of the sulfur, and must involve little change in existing equipment. In addition, a successful process must not affect the quality or quantity of coke produced.

In the preceding paper the reactions which coal sulfur undergoes during carbonization have been described. From these experiments it was concluded that pyrite decomposed to form ferrous sulfide or pyrrhotite and hydrogen sulfide, the ratio between the residual sulfur and the volatile sulfur being about 1 : 1. Secondary reactions at the higher temperatures of the coking process cause the ferrous sulfide to change over partly to what is apparently a "carbon-sulfur" compound.[5] The organic sulfur completely decomposes, more than one-half being retained in the coke in an altered form, while the remainder is evolved as hydrogen sulfide, together with small quantities of thiophene or other volatile organic compounds. The resulting sulfur of the coke will consist, therefore, of iron sulfide, either as ferrous sulfide or as pyrrhotite, and a larger quantity of a very stable organic sulfur substance. The percentage of organic sulfur in the coke is higher than that of the

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[1] Published by permission of the Director of the U. S. Bureau of Mines.

[2] Presented by title at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

[3] T. Fraser and H. F. Yancey, *Bull. Am. Inst. Mining Eng.*, **1919**, 1817.

[4] Alfred R. Powell, THIS JOURNAL, **12** (1920), 1069.

[5] Groves and Thorp, "Chemical Technology," **1**, p. 123. J. and A. Churchill, London, **1889**.

[6] D. R. P. 261,361, May 2, 1912.

[7] Groves and Thorp, *Loc. cit.*

[8] U. S. Patent 887,145, May 12, 1908.

[1] D. R. P. 270,573, June 7, 1913.

[2] Groves and Thorp, *Loc. cit.*

[3] U. S. Patent 1,007,153, October 31, 1911.

[4] D. R. P. 274,853, April 12, 1912.

[5] References in this paper to a "carbon-sulfur" compound and to organic sulfur in coke are simply convenient terms to designate a combination or existence of sulfur in coke as yet unknown. Indications point to the association of this sulfur with the carbon of the coke, but whether this is a physical or a chemical association is as yet undetermined.

TABLE I—SOURCE AND PROXIMATE AND SULFUR ANALYSES OF COALS[1]

Laboratory Number	Name	Source	Moisture	Volatile Matter	Fixed Carbon	Ash	Sulfur
18847	Pittsburgh	Pennsylvania, Bruceton, Experimental Mine, Bureau of Mines	1.57	38.72	54.95	4.75	1.72
23066	Upper Freeport	Pennsylvania, Butler Co., Cunningham Coal Company	2.04	33.11	56.36	8.49	1.21
33945	Joliet coking	Pocahontas, 65%; Lynch, Ky., 20%; Franklin Co., Ill. (washed), 15%. As charged in by-product ovens, Illinois Steel Co., Joliet, Ill.	0.92	26.28	65.60	7.20	0.82

[1] All samples in an air-dry conditon.

inorganic sulfur; hence, the former is the substance to be attacked in a desulfurization process.

One means of accomplishing desulfurization would be to modify the sulfur reactions of the coking process so as to secure larger amounts of the volatile sulfur compounds and less of the residual. Another method would be to attack the sulfur of the finished coke in an attempt to secure its removal. The process developed in this investigation could be used in either way, but it is more convenient to apply the necessary methods during the carbonization period.

Some time ago a method was proposed for the determination of total sulfur in coke by the use of nascent hydrogen.[1] This method has never come into extensive use for the purpose for which it was intended, but is interesting as showing the comparative ease with which the stable sulfur in coke may be eliminated. The powdered coke was mixed with zinc or aluminium foil, and heated in water, and hydrochloric acid was added. Most of the sulfur was eliminated as hydrogen sulfide, although the author has never found that the method completely converts the sulfur into hydrogen sulfide.

Since nascent hydrogen has such a decided effect on the coke sulfur, it was thought that hydrogen passed through the coking mass might show a material desulfurizing action. If this were so, the process might find extensive commercial application, since the lean gases produced by the carbonization of coal contain about 50 per cent of hydrogen. Thus a by-product could be utilized for the desulfurization which would not injure the coke, and, furthermore, the by-product gas itself would not be changed essentially.

EXPERIMENTAL METHOD

All the experimental work described in this paper has been done in a very small laboratory apparatus. The process is now being applied on a larger scale, using a 10-lb. charge; if these experiments are successful, tests will be made in commercial coke ovens.

The apparatus was essentially the same as that used in the study of reactions of coal sulfur during the coking process, and fully described in the paper already referred to.

The coking charge consisted of 5 g. of coal contained in a fused silica tube. This tube was heated by an electric tube furnace with the temperature under close control at all times. Hydrogen was admitted to the inlet end of the coking tube through a flowmeter, so that the rate of flow could be maintained fairly constant. The supply of hydrogen was furnished by a Kipp generator, which gave a uniform rate of flow. The outlet end of the tube contained a cotton plug for a tar filter, and was connected to a flask containing ammoniacal cadmium chloride to collect the hydrogen sulfide evolved. At the end of the coking process the contents of the cadmium chloride flask were acidified, and the hydrogen sulfide determined iodometrically.

The coke was pulverized and treated with dilute hydrochloric acid, by which means the sulfur combined as sulfide was evolved as hydrogen sulfide, which was absorbed in cadmium chloride and titrated with iodine.

The residue from the hydrochloric acid extraction was treated with nitric acid (sp. gr. 1.12) for 24 hrs. at room temperature to extract any pyrite that might remain, then filtered, the filtrate evaporated to dryness, and sulfur and iron determined by the usual methods. By comparison of these analyses with those of the corresponding tests where no hydrogen was used, the efficiency of hydrogen as a desulfurizing agent could be estimated. In most cases the determination of the hydrogen sulfide evolved, as the measure of desulfurization, was checked by actual determination of the sulfur in the coke.

DESCRIPTION OF COALS

Three coals were used in this investigation. Table I gives the laboratory sample number, the name to be used in referring to the coal, a brief description of its source, and the results of proximate and sulfur analyses.

RESULTS OF EXPERIMENTS

PITTSBURGH COAL—The Pittsburgh coal was completely carbonized by being kept in the tube furnace for 2 hrs. at 1000°. It had been found by previous tests that the coal sulfur reaches a condition of stability under these conditions, and that no more hydrogen sulfide will be evolved by keeping the coke at this temperature for a longer period. Pure hydrogen was then passed through the furnace at the rate of 100 cc. per minute for a period of one hour.[1] Comparative figures on the coke sulfur before and after the treatment with hydrogen are given in Table II.

TABLE II—DESULFURIZATION OF COKE FROM PITTSBURGH COAL BY HYDROGEN

	Without Hydrogen	With Hydrogen
Total sulfur in coal (Per cent air-dry coal)....	1.72	1.72
Sulfur evolved as hydrogen sulfide (Per cent air-dry coal)........	0.53	0.74
Sulfur in coke (Per cent air-dry coal)..........	1.14	0.93
Sulfur in coke (Per cent air-dry coke)..........	1.90	1.55

In interpreting these results, it must be kept in mind that the hydrogen was passed through the finished coke after, and not during, its formation. The sulfur analysis of this coal shows that out of the total sulfur percentage of 1.72, 0.79 per cent is combined as pyrite, 0.23 per cent as sulfate, and 0.70 per cent as organic sulfur. The large amount of sulfide sulfur in the coal accounts for the high sulfur coke from the ordinary distillation. The flow of hydrogen for one hour brought the coke sulfur from 1.90 down to 1.55 per cent.

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[1] N. Oteha, *Z. angew. Chem.*, **1897**, 330.

[1] A flow of hydrogen of 100 cc. per minute for one hour through 5 g. of coal would mean 38 M cu. ft. per ton of coal. It must be remembered that the coal rested in the bottom of the tube in the laboratory apparatus, and the majority of the hydrogen simply passed over without accomplishing any desulfurization. For this reason there can be no comparison between laboratory conditions and actual coke-oven practice, so far as the amount of hydrogen required is concerned.

The coke was now cooled from 1000° to 500° C., and the flow of hydrogen continued. Under these conditions, no hydrogen sulfide was obtained, showing that no desulfurization took place on the finished coke at this temperature. On raising the temperature again to 1000°, evolution of hydrogen sulfide continued at the same rate as before.

Tests on the Pittsburgh coal were continued and the hydrogen was passed through continuously from the start of the carbonization, at a rate of 100 cc. per minute. After 2 hrs. at 500°, it was found that 1.6 times as much hydrogen sulfide had been evolved as in a corresponding test without the use of hydrogen. The charge was then slowly carried up to 1000° over a period of 2 hrs. Table III shows the effect of the 4 hr. flow of hydrogen, as compared with a coking test where no hydrogen was used.

TABLE III—DESULFURIZATION BY HYDROGEN IN COKING TEST OF PITTSBURGH COAL

	Without Hydrogen	With Hydrogen
Total sulfur in coal (Per cent air-dry coal)	1.72	1.72
Sulfur evolved as hydrogen sulfide (Per cent air-dry coal)	0.53	1.15
Sulfide sulfur in coke (Per cent air-dry coal)	0.16	0.08
Total sulfur in coke (Per cent air-dry coal)	1.14	0.52
Total sulfur in coke (Per cent air-dry coke)	1.90	0.86

Actual analysis of the sulfur in the coke checked within a few hundredths of a per cent with that given above by difference. The result of this experiment was a reduction of sulfur in the coke from 1.90 to 0.86 per cent, or a decrease of considerably over one-half. This reduction was obtained from a coal containing sulfur of a very nonvolatile nature, as shown by the high sulfur content of the coke as compared with the coal.

Further experiments with the Pittsburgh coal in which the hydrogen was mixed with a small quantity of moist hydrochloric acid vapor gave results agreeing closely with those given above. As a matter of fact, the total sulfur in this coke was a little higher than in the coke from the straight hydrogen run, although the sulfide sulfur was a little lower. The addition of a small quantity of hydrochloric acid vapor cannot, therefore, be regarded as assisting desulfurization.

UPPER FREEPORT COAL—Two runs were made to determine the effect of hydrogen on the desulfurization of the Upper Freeport coal. One of these was made at 500° for 2 hrs. with the hydrogen flowing at the rate of 100 cc. per minute. The other was made at 500° for one hour, and then at 1000° for an hour, with the hydrogen flow at 100 cc. per minute. This latter run was made with the hydrogen slightly moist, since this seems to favor desulfurization. Analyses of the products were made by the methods described in the previous paper.[1] A summary of the results, together with the corresponding results obtained without the use of hydrogen, is given in Table IV.

TABLE IV—DISTRIBUTION OF SULFUR WITH AND WITHOUT HYDROGEN IN UPPER FREEPORT COAL, No. 23066

(Values given in per cent of original air-dry coal)

		Without Hydrogen		With Hydrogen	
	Coal	500° C.	1000° C.	500° C.	1000° C.
Pyritic sulfur	0.47	0.33	0.00	0.01	0.00
Sulfate sulfur	0.07	0.01	0.00	0.01	0.00
Organic sulfur	0.67	0.58	0.66	0.63	0.07
Sulfide sulfur	0.00	0.09	0.12	0.17	0.00
Sulfur evolved as H_2S	0.00	0.17	0.40	0.36	1.11
Tar sulfur	0.00	0.03	0.03	0.03	0.03
Total sulfur	1.21	1.21	1.21	1.21	1.21

The sulfur left in the coke at 1000° is the sum of the organic sulfur and the sulfide sulfur. If the percentages given above on the basis of the original coal are figured to the percentage of sulfur in the coke, the coke produced without hydrogen contains 1.20 per cent sulfur, while the coke made with the hydrogen contains 0.11 per cent sulfur. There has therefore been a reduction of over 90 per cent of the coke sulfur due to the effect of the hydrogen. This was the highest reduction obtained by the use of hydrogen during the coking process. The passage of the hydrogen seemed to produce no effect on the character of the coke, other than to remove the sulfur, although the coke produced from this coal was rather fragile and crumbly both with and without hydrogen treatment.

From the data given in Table IV, the reactions which the various forms of sulfur had undergone during the coking process were calculated on a basis which has been discussed in the previous paper. The figures (in Table V) to express the magnitude of the reactions are in terms of per cent of sulfur reacting, on the basis of the weight of the original air-dried coal.

TABLE V—REACTIONS OCCURRING IN CARBONIZATION OF UPPER FREEPORT COAL

(Results expressed in per cent sulfur on basis of air-dry coal)

Temperature Range, ° C.	$FeS_2 = FeS + H_2S$	$MSO_4 = MS$	Organic S $= H_2S$	Organic S = Tar S	MS = Organic S
WITHOUT HYDROGEN					
0–500	0.14	0.06	0.10	0.03	0.04
500–1000	0.33	0.01	0.06	0.00	0.14
WITH HYDROGEN					
0–500	0.46	0.06	0.13	0.03	0.12
500–1000	0.01	0.01	0.88	0.00	0.18

A study of Table V shows that three of the five reactions are modified by the presence of hydrogen. The coal pyrite is caused to decompose at a lower temperature, the decomposition being practically complete at 500°; whereas without the hydrogen, less than one-third of the sulfur had been affected below 500°. This was to be expected, since the speed of decomposition of pyrite is determined not only by the temperature, but also by the partial pressure of free sulfur over it. The presence of an excess of hydrogen keeps the amount of free sulfur down to an almost negligible quantity. It should be pointed out here that the modification of this pyrite decomposition reaction does not assist the desulfurization process directly, since no more sulfur elimination is secured than in the case of ordinary distillation, but this sulfur elimination occurs during an earlier stage of the carbonization.

The entire desulfurizing effect of the hydrogen is due to the increased conversion of organic sulfur into hydrogen sulfide. A comparison of the figures on this reaction shows that below 500° the increased elimination of sulfur due to the hydrogen is very slight, but that above 500° the difference is enormous. This bears out the conclusions reached previously, namely, that desulfurization by hydrogen is most active at the higher temperatures of the coking process.

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[1] *Loc. cit.*

The third reaction affected by the passage of hydrogen through the coking mass is the fixing of the sulfide sulfur in some combination with carbon or coke substance. The changes in the extent of this reaction are secondary and are not caused directly by the hydrogen, but are due to a mass-action effect. Below 500° hydrogen causes an increased decomposition of pyrite, thus making an increased amount of ferrous sulfide, which by mass action increases the extent of this particular reaction. Above 500° the constant elimination of the organic sulfur as hydrogen sulfide also tends to increase the extent of the reaction by decreasing the resulting product of the reaction.

This conversion of the sulfide sulfur into a "carbon-sulfur" combination must be regarded as of considerable assistance in the desulfurization process, although it in itself does not cause the elimination of sulfur from coke. Hydrogen does not react with hot ferrous sulfide[1] although it will react very readily with the "carbon-sulfur" combination of the coke. This reaction, therefore, carries the ferrous sulfide to an easily eliminated form of sulfur.

USE OF BY-PRODUCT GAS—The experiments so far described have been carried out with pure hydrogen. Since any possible practical use of the process would be carried out with the by-product gas from the coking operation, it was desired to determine the desulfurizing effect of such a gas. The gas made for this purpose had the following approximate composition by volume.

	Per cent
Hydrogen	50.0
Methane	25.0
Carbon monoxide	15.0
Air, CO_2, etc	10.0
TOTAL	100.0

This gas, which corresponds very closely to an average lean coke-oven gas, at least in the content of hydrogen, was passed through the Upper Freeport coal at the same rate and under exactly the same conditions as the hydrogen had been. The results are given in Table VI, together with comparative results from the ordinary distillation, and the distillation with pure hydrogen.

TABLE VI—SULFUR ELIMINATED AND SULFUR RETAINED IN COKE UNDER DIFFERENT CONDITIONS OF DISTILLATION—UPPER FREEPORT COAL

(Total sulfur 1.21 per cent)

	Sulfur Eliminated as H_2S (Per cent on Basis of Air-Dry Coal)				Sulfur in Coke
	1 hr.	1.5 hrs.	2 hrs.	3 hrs.	Per cent
Ordinary distillation	0.17	....	0.40	....	1.20
By-product gas purge	0.40	....	0.86	0.96	0.34
Hydrogen purge	0.72	1.02	1.11	....	0.11

The elimination of hydrogen sulfide under the different conditions of distillation is shown graphically in Fig. 1. From these comparative results it appears that a 50 per cent hydrogen mixture is much slower in its desulfurizing action, and in practice would never reach the degree of desulfurization attained by the pure hydrogen. Nevertheless, the sulfur removal by the by-product gas is decided, as shown by the reduction in coke sulfur from 1.20 per cent to 0.34 per cent.

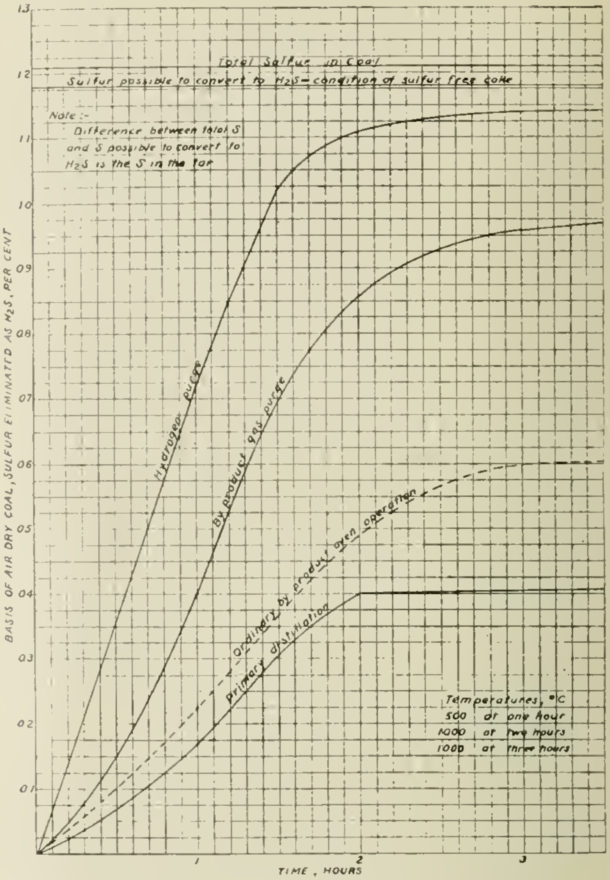

FIG. 1—CURVES SHOWING ELIMINATION OF SULFUR AS HYDROGEN SULFIDE FROM UPPER FREEPORT COAL, NO. 23066, WHEN COKED UNDER DIFFERENT CONDITIONS. IN PRIMARY DISTILLATION NO HYDROGEN-CONTAINING GAS IS PASSED THROUGH

JOLIET COKING COAL—In Table VII are given the data on the passage of hydrogen through the Joliet coking coal for a 3-hr. period. This run differed from the others in that the coal was not pulverized to 100-mesh size, but was of mostly 10-mesh size.

TABLE VII—DESULFURIZATION BY HYDROGEN IN COKING TEST OF JOLIET COAL

	Without Hydrogen	With Hydrogen
Total sulfur in coal (Per cent air-dry coal)	0.82	0.82
Sulfur as hydrogen sulfide (Per cent air-dry coal)	0.25	0.59
Total sulfur in coke (Per cent air-dry coal)	0.55	0.21
Total sulfur in coke (Per cent air-dry coke)	0.75	0.29

It is to be noted that the sulfur of the coke was reduced from 0.75 to 0.29 per cent, even with the coal in comparatively coarse granules. Another run with the coal ground to 100 mesh did not show even as good sulfur elimination as the coarser size. Since the coal has entirely fused into one mass at the temperatures at which desulfurization takes place (500° to 1000°), the state of subdivision of the original coal should not affect the desulfurizing process materially.

The coke made from the Joliet coking coal as produced in the by-product ovens contains 0.64 per cent sulfur. The coke made in the laboratory from the same coal contains 0.75 per cent sulfur, the difference being due to the purging effect of the by-product gases passing through the red-hot coke in the oven. A test, to determine how much the finished coke from the by-product oven could be desulfurized by heating to 1000° and passing hydrogen through for one hour, resulted in a reduction in the coke sulfur from 0.64 to 0.50 per cent, showing that desulfurization of coke by hydrogen was not limited to the actual coking process.

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[1] Roscoe and Schlorlemmer, "Treatise on Chemistry," Macmillan & Co., London, **1907**, Vol. II, p. 1208.

CONCLUSIONS

A study has been made of the efficiency of hydrogen and gases containing hydrogen as desulfurizing agents, when passed through finished coke at high temperatures or through coal in the process of coking.

The effect of hydrogen on the removal of sulfur from coke is very noticeable, in most cases the majority of the sulfur being removed during a period of 3 hrs. at 1000° C. With the exception of the decrease in sulfur content, the character of the coke does not seem to be affected by the passage of hydrogen.

Three of the sulfur coking reactions are modified by the passage of hydrogen through the coking mass.

(1) Coal pyrite, FeS_2, is caused to decompose at a lower temperature, the decomposition being practically complete at 500°. This change of speed of reaction does not affect the final desulfurization results, however, since complete decomposition of the pyrite is finally attained in the ordinary coking process.

(2) The decomposition of organic sulfur to form hydrogen sulfide is very little affected below 500°, but is enormously increased from 500° to 1000°. All of the desulfurizing effect of the hydrogen is due to this increased decomposition.

(3) A larger amount of sulfide is converted to a "carbon-sulfur" combination. This is due to mass action and results from the modifications in the two reactions given above.

Gaseous mixtures containing hydrogen, such as coke-oven gas, are slower in their desulfurizing action, and even with a longer time of exposure would probably never give the degree of desulfurization attained by the use of pure hydrogen. Their efficiency for the removal of sulfur from coke is high, however, and the repassing of by-product gas through the coking mass may prove of commercial value.

The original state of subdivision of the coal does not affect the desulfurization process. This is because the coal fuses between 350° and 400°, while desulfurization begins above 500°.

The coke produced in coke ovens contains less sulfur than would be accounted for by the primary coking reactions. This is due to the flow of the by-product gas produced through the coking mass.

ACKNOWLEDGMENTS

The author wishes to express his appreciation for suggestions and other valuable assistance during this investigation to Mr. E. A. Holbrook, superintendent, Mr. A. C. Fieldner, supervising chemist (under whose general direction the investigation was conducted), and Mr. J. D. Davis, chemist, of the Pittsburgh Station, Bureau of Mines; and to Messrs. J. R. Campbell, chief chemist, H. C. Frick Coke Co., J. V. Freeman, chief chemist, Central Laboratory, Illinois Steel Co., and others who have been interested in the work as it progressed.

NAPHTHALENE SULFONIC ACIDS. I—SOME DIFFICULTLY SOLUBLE SALTS OF CERTAIN NAPHTHALENE SULFONIC ACIDS[1]

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In the course of the investigation of the sulfonation products of naphthalene, it became of interest to make and study as many as possible of the more difficultly soluble salts of those acids which might be formed by direct sulfonation, *viz.*, the α- and β-monosulfonic acids and the 1,5-, 1,6-, 2,6- and 2,7-disulfonic acids of naphthalene. The purpose of investigating these salts was to obtain a characteristic salt of each acid which might serve as the basis of a qualitative test for that acid.

The known difficultly soluble inorganic salts of these acids were found unsuited for the purpose in hand, with the exception of the salts of naphthalene-β-sulfonic acid with the heavier metals; such as the nickel, cobalt, copper, cadmium, zinc, and silver salts described by O. N. Witt,[3] and the ferrous salt,[4] known in the industries but not described in any scientific work so far as the author can find.

Erdmann and Süvern[5] are the only ones who have recorded work on the salts of these acids with organic bases. They describe the salts of the α-, β-, 2,6- and 2,7-sulfonic acids with aniline, benzidine, and *o*-tolidine, but give no analyses of the salts formed.

To investigate this class of salts more thoroughly, salts of various organic bases with the six sulfonic acids were prepared, and those that were difficultly soluble were studied further. The most important of these are described here, and some of their uses in the following paper. Other difficultly soluble salts will probably be described in later contributions from this laboratory.

The method of making the salts was the same in each case. Molecularly equivalent quantities of the acid, or its sodium or potassium salt, and the hydrochloride of the organic base were dissolved separately in hot water, and the two solutions mixed, stirred thoroughly, and allowed to cool. The crystallized salts were filtered, washed with cold water, and dried in a vacuum oven at 100°.

Since they are salts of strong acids with weak bases, they are all easily hydrolyzed by boiling water. In attempting to recrystallize them, a little of the hydrochloride of the base should always be added to counteract this change.

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[1] Presented at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

[2] Crystallographic-optical data by Edgar T. Wherry.

[3] *Ber.*, **48** (1915), 743.

[4] Cain, "Manufacture of Intermediate Products for Dyes," p. 166; Brit. Patent 4459 (1894).

[5] *Ann.*, **275** (1893), 297.

The sulfur in all of these salts was determined as follows: An amount of the salt not exceeding 200 mg. was ignited in a Parr calorimeter bomb with about 5 g. of sodium peroxide. The ignition mass was dissolved in water, the solution acidified, and sulfuric acid was determined as usual by precipitation with barium chloride.

α-NAPHTHYLAMINE NAPHTHALENE-α-SULFONATE,

$C_{10}H_7NH_2.C_{10}H_7SO_3H$

This salt separates, on cooling the hot solution, in well-defined, glistening, micaceous leaflets, generally arranged in groups. It is soluble in hot water, in hot 95 per cent alcohol, and in a cold mixture of 4 volumes of alcohol and 1 of water, but is practically insoluble in cold water and alcohol and in acetone. It melts with decomposition at 232°. Upon analysis, 9.09 and 9.34 per cent of sulfur were found, with the calculated value at 9.13 per cent.

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES.[1] *Crystal habit*—When examined under the microscope in ordinary light seen to be made up of overlapping plates.

Refractive indices (for D)—[Determined by inserting the polarizer (sub-stage nicol prism) and immersing a small amount of the substance on a microscope slide in liquids of known refractive index one after another until the crystals lying in some definite position disappear, because their index is matched; and repeating for crystals lying in other positions.]

$\alpha = 1.552$, β not determined, $\gamma = 1.795$, $\gamma - \alpha = 0.243$, all ± 0.005; indices α and γ usually shown.

Features shown in parallel polarized light, with nicols crossed—Double refraction extreme, the colors being first to second order, often in beautiful mosaics, on thin plates, but ranging up to fourth or fifth order on thick or upturned ones; extinction parallel to occasional edges; elongation indefinite.

Features shown in convergent polarized light, with nicols crossed—None.

Diagnostic features—The features likely to be of greatest use in identifying this substance are the crystal habit and the value of the lowest refractive index, α. If immersed in nitrobenzene ($n_D = 1.552$) or another oily liquid with about the same n, and examined under the microscope with the polarizer in, the plates disappear practically completely when the direction of index α lies parallel to the plane of vibration of the polarizer.

β-NAPHTHYLAMINE NAPHTHALENE-α-SULFONATE,

$C_{10}H_7NH_2.C_{10}H_7SO_3H$

This salt crystallizes on cooling from dilute hot solutions in large, glistening, micaceous, diamond-shaped plates. If the hot solution is too concentrated, it forms on cooling a stiff jelly resembling slightly cooked egg albumen. This jelly-like form may partially change, on standing, into a mass of long colorless needles. If this jelly-like form is heated with more water, it dissolves, and the plates are formed on cooling.

The plates are difficultly soluble in cold water, acetone, and 95 per cent alcohol; but soluble in hot water, hot acetone, hot alcohol, and in a cold mixture of 4 volumes of alcohol and 1 of water. The salt blackens at 202° and melts at 211°. Analyses gave 9.08 and 8.98 per cent sulfur (theory, 9.13).

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES. *Crystal habit*—Elongated plates, sometimes showing a 125° termination.

Refractive indices (D)—$\alpha = 1.620$, $\beta = 1.670$, $\gamma =$ greater than 1.850, $\gamma - \alpha = 0.23+$, all ± 0.005; indices α and β are usually shown.

In parallel polarized light—Double refraction extreme, the colors being first to second order, sometimes in confused mosaics, on thin plates; extinction parallel to prominent edges; elongation +.

In convergent polarized light—A biaxial figure frequently shown, the sign being + and $2\,E = 85° \pm 5°$.

Diagnostic features—The features most useful for identifying this substance are the crystal habit, value of the intermediate index, β, and sign of elongation. The immersion liquid may best consist of a mixture of 5 parts α-monobromonaphthalene with 1 part methylene iodide. When crystals are turned so that their longest dimension lies parallel to the plane of vibration of the polarizer, they disappear in this liquid, showing their elongation to be + in sign and the index to be 1.670.

α-NAPHTHYLAMINE NAPHTHALENE-β-SULFONATE,

$C_{10}H_7NH_2.C_{10}H_7SO_3H$

This salt forms a voluminous white precipitate in the hot solution, which is made up of microscopic needles. It is soluble in a cold mixture of 4 volumes of alcohol and 1 of water, considerably soluble in hot water and hot 95 per cent alcohol, difficultly soluble in cold water, cold 95 per cent alcohol, and hot and cold acetone. It melts with decomposition at 240° to 242°. The per cent of sulfur found was 9.08 and 9.29 (theory, 9.13).

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES. *Crystal habit*—Needles.

Refractive indices (D)—$\alpha = 1.600$, $\beta = 1.650$, $\gamma = 1.725$, $\gamma - \alpha = 0.125$, all ± 0.005; index γ usually shown lengthwise, and means of α and β crosswise.

In parallel polarized light—Double refraction extreme, bright first order colors being shown even on very minute grains; extinction parallel; elongation +.

In convergent polarized light—.........

Diagnostic features—The features most useful in identifying this substance are the crystal habit, value of highest index, and sign of elongation. The immersion liquid may best consist of a mixture of 5 parts methylene iodide with 1 part α-monobromonaphthalene. When the needles are turned so that their long dimension lies parallel to the plane of vibration of the polarizer, they disappear in this liquid, showing their elongation to be + in sign and the highest index to be 1.725.

β-NAPHTHYLAMINE NAPHTHALENE-β-SULFONATE,

$C_{10}H_7NH_2.C_{10}H_7SO_3H$

This salt also forms insoluble microscopic plates in the hot solution. It is slightly soluble in hot water and 95 per cent alcohol, considerably soluble in a cold, and easily soluble in a hot mixture of 4 volumes of alcohol and 1 of water, slightly soluble in cold alcohol, and difficultly soluble in cold water and in acetone. It melts with decomposition at 276° to 279°. It contained 9.00 and 9.10 per cent of sulfur (theory 9.13).

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES. *Crystal habit*—Minute plates (or rods), with irregular wavy structure.

Refractive indices (D)—$\alpha = 1.640$, $\beta = ?$, $\gamma = 1.730$, $\gamma - \alpha = 0.090$, all ± 0.005; index α usually shown in one direction.

In parallel polarized light—Double refraction extremely strong, first to second order colors being shown even on very minute plates; extinction and elongation indeterminate.

In convergent polarized light—Traces of a biaxial figure occasionally shown, but the crystals are too minute for its measurement.

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[1] The authors herewith acknowledge the aid of Mr. George L. Keenan of this Bureau in checking some of these data.

Diagnostic features—The feature most useful in identifying this substance is the unusually high value of the lowest index, α. This index is almost exactly matched by α-monochloronaphthalene (n_D = 1.639), and most of the crystals disappear in one direction or another when immersed in this liquid. For confirmative purposes the other indices may be determined in similar manner, using mixtures of this liquid with methylene iodide of the indices above stated.

FERROUS NAPHTHALENE-β-SULFONATE, $Fe(C_{10}H_7SO_3)_2.6H_2O$[1]

The author makes no claim to the discovery of this salt which has been extensively made and used in industrial plants. A description of it is given here, since no reference has been found in scientific literature or elsewhere than in the British patent.

The salt separates in large, glistening, colorless, micaceous plates, when ferrous chloride is added to a cold solution of naphthalene-β-sulfonic acid or its salts. It is difficultly soluble in cold, but readily soluble in hot water. It is remarkably stable, not being oxidized to any appreciable extent by exposure to air. At 150° to 160° all the water of crystallization is removed and the salt becomes yellowish brown, probably due to slight superficial oxidation of the iron.

Analysis	Calculated Per cent	Found Per cent	
Iron	9.67	9.52	9.53
Water	18.69	18.50	....

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES. *Crystal habit*—Plates, sometimes showing a 140° termination.

Refractive indices (D)— α = 1.500, β not determined, γ = 1.660, $\gamma - \alpha$ = 0.160, all ±0.005; indices α and γ usually shown.

In parallel polarized light—Double refraction extreme, second order colors being shown even on thin plates; extinction parallel to crystal edges occasionally present; elongation indeterminate.

In convergent polarized light—Partial biaxial figure occasionally shown, the axial angle being large and the sign apparently +.

Diagnostic features—The feature most characteristic of this substance is the unusually low value of the lowest index, α. The immersion liquid may be benzene (n_D = 1.499), or another liquid of about the same n (for instance, some grades of lubricating oil). Most of the crystals disappear in one direction or another when immersed in this liquid. The other properties may be used for confirmation.

α-NAPHTHYLAMINE NAPHTHALENE-1,5-DISULFONATE, $(C_{10}H_7NH_2)_2.C_{10}H_6(SO_3H)_2$

This salt is almost completely insoluble in boiling water. It forms a heavy precipitate of a poorly defined, granular, platy nature. It is very slightly soluble in hot water, 95 per cent alcohol, and a mixture of 4 volumes of alcohol and 1 of water, and practically insoluble in these solvents in the cold, and in acetone. It does not melt below 280°. Analyses gave 10.94 and 10.97 per cent sulfur (theory 11.16).

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES. *Crystal habit*—Plates, irregular in outline.

Refractive indices (D)— α = 1.600, β not determined, γ = 1.795, $\gamma - \alpha$ = 0.195, all ±0.005; indices α and γ often shown.

In parallel polarized light—Double refraction extreme, second order colors being shown even on very thin plates; extinction apparently inclined; elongation indeterminate.

In convergent polarized light—Partial biaxial figures rarely shown.

Diagnostic features—The value of the lowest refractive index, α, is characteristic of this substance, when considered in connection with its habit. One other compound in the series studied, α-naphthylamine naphthalene-β-monosulfonate, has the same α value, but it crystallizes in needles, and is thus readily distinguishable. For immersion, a mixture of equal parts of bromobenzene and α-monochloronaphthalene (n_D = 1.600) may be used. The crystals will disappear in one direction or another in this liquid.

β-NAPHTHYLAMINE NAPHTHALENE-1,5-DISULFONATE, $(C_{10}H_7NH_2)_2.C_{10}H_6(SO_3H)_2$

This salt precipitates from the boiling solution in a dense voluminous mass of small plates. It is only slightly soluble in hot water and alcohol, and practically insoluble in cold solvents, being slightly more soluble in mixtures of 4 volumes of alcohol and 1 of water. It does not melt below 280°. The results of sulfur determinations were 11.12 and 11.23 per cent (theory 11.16).

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES—Unless care is taken to have an excess of base present, there is a strong tendency for another substance, apparently an acid salt, to crystallize out along with this compound. It has so far been impossible to obtain this other substance in a pure form and no analytical data can be given at present. The acid salt has highly distinctive optical properties, and can be readily recognized when studied under the microscope, but if the two are intimately mixed difficulties may be encountered in confirming the identity of the normal salt. The properties of both are here given.

Normal salt. Crystal habit—Plates, irregular in outline.

Refractive indices (D)— α = 1.631, β = 1.647, γ = 1.755, $\gamma - \alpha$ = 0.124, all ±0.005; indices α and β are usually shown, but γ is exhibited on uptilted plates.

In parallel polarized light—Double refraction extreme, bright first order colors being shown on extremely thin plates; extinction and elongation indeterminate.

In convergent polarized light—Biaxial figures frequently shown, the sign being +, and 2 E = 75° ±5° (2 E calculated from ns = 77° 06′).

Diagnostic features—The features most useful in identifying this substance are the values of the two lower refractive indices, α and β, and the readiness with which an interference figure can be obtained. In a mixture of 3 parts α-monobromonaphthalene with one part monobromobenzene (n_D = 1.632) practically all of the plates disappear in one direction or the other; and in pure α-monobromonaphthalene (n_D = 1.656) they also disappear. On introducing the substage condenser, using a 4 mm. objective, crossing the nicol prisms, and removing the eyepiece, a fairly distinct biaxial interference figure will usually be seen, the dark brushes lying well within the field. If the microscope is provided with means for measuring axial angles, the numerical value can be obtained; if not, repetition of the procedure, using a thin flake of muscovite mica, will give a figure of practically identical dimensions, showing the axial angle to be not far from 75°.

Acid salt—This is distinguished from the normal salt by the extraordinarily strong double refraction, which exceeds 0.30, the value of α being 1.550, and that of γ being higher than the highest immersion liquid available, the n of which is 1.850. (β = 1.700.) As a result, the plates of this substance show third or fourth order colors, even when very thin. The axial angle, 2 E, is also much larger than is that of the normal salt, so that the dark brushes do not appear in the field of view when the interference figure lies in the diagonal position. These features differentiate this acid salt not only from the corresponding normal salt, but also from all other compounds of the series here studied; and the acid salt, if obtained, can therefore be recognized and excluded from consideration promptly.

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[1] Boulton, Haywood, Boulton, and Fergusson, Brit. Patent 4459 (1894).

α-NAPHTHYLAMINE NAPHTHALENE-1,6-DISULFONATE, $(C_{10}H_7NH_2)_2.C_{10}H_6(SO_3H)_2$

This salt separates in long, slender needles on cooling a hot solution. It is soluble in hot water, 95 per cent alcohol, soluble in cold mixtures of 4 volumes of alcohol and 1 of water, slightly soluble in cold alcohol, and practically insoluble in cold water and in acetone. It decomposes at 265° to 267°. The value found for sulfur was 11.25 and 11.22 per cent (theory 11.16).

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES. *Crystal habit*—Well-defined rods, probably belonging to the monoclinic system.

Refractive indices (D)— $\alpha = 1.583$, $\beta = 1.730$, $\gamma = 1.770$, $\gamma - \alpha = 0.187$, all ± 0.005; index α is usually shown lengthwise, and γ crosswise, of the rods; β is sometimes shown crosswise, especially on rods so turned as to show parallel extinction.

In parallel polarized light—Double refraction extreme, the colors being second to third order, even on fairly slender rods; extinction inclined, at an angle of 17° ± 1°; elongation negative.

In convergent polarized light—Partial biaxial figure occasionally shown, the sign being —, and 2 E large.

Diagnostic features—The features most useful in identifying this substance are the value of the lowest refractive index, α, and the inclined extinction seen in parallel polarized light, with the nicol prisms crossed. The immersion liquid may consist of aniline, which has $n_D = 1.585$, which lies so near to the value of α for this substance that the rods disappear practically completely when immersed in it and turned to the appropriate position. To determine how they should lie in order that this effect shall be shown, each rod should first be examined under crossed nicols, and the stage turned until extinction occurs. If the stage is graduated, this will be found to be the case when the crystal lies at about 17° from parallelism with one or the other cross hair. On throwing out the analyzer, the rods lying near the cross hair indicating the plane of vibration of the polarizer will disappear.

β-NAPHTHYLAMINE NAPHTHALENE-1,6-DISULFONATE, $(C_{10}H_7NH_2)_2.C_{10}H_6(SO_3H)_2$

This salt forms long, flat, silky needles when crystallized from hot water. It is soluble in hot water, 95 per cent alcohol, slightly soluble in cold alcohol, and practically insoluble in cold water and in acetone. It is soluble in a cold mixture of 4 volumes of alcohol and 1 volume of water. It does not melt below 280°. On analysis it gave 10.97 and 11.03 per cent sulfur (theory 11.16).

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES. *Crystal habit*—Needles.

Refractive indices (D)— $\alpha = 1.550$, $\beta = 1.700$, $\gamma = 1.755$, $\gamma - \alpha = 0.205$, all ± 0.005; index α usually shown lengthwise, and means between the others crosswise of the needles.

In parallel polarized light—Double refraction extreme, the colors being third or fourth order even on slender needles; extinction parallel; elongation negative.

In convergent polarized light—Partial biaxial figures sometimes shown, the sign being apparently —, and 2 E large.

Diagnostic features—The features most useful in identifying this substance are the habit, the value of the lowest refractive index, α, and the extinction. None of the other members of the β-naphthylamine series studied crystallize in needles, although one (the 2,7-compound) is, to be sure, in rods; but this other substance differs sharply in the other two respects mentioned. The immersion liquid may best consist of nitrobenzene, or other oily liquid with n_D around 1.55. The needles disappear completely when immersed in this liquid and turned so that their long direction lies parallel to the plane of vibration of the polarizer. They also extinguish in the same position when the analyzer is inserted. The rods of the 2,7-compound, on the other hand, do not disappear in this liquid, and extinguish when lying at an angle of about 10° with a cross hair.

α-NAPHTHYLAMINE NAPHTHALENE-2,6-DISULFONATE, $(C_{10}H_7NH_2)_2.C_{10}H_6(SO_3H)_2$

This salt separates in minute needles and lumps when a hot solution is cooled. It is moderately soluble in hot water, slightly soluble in hot 95 per cent alcohol, and practically insoluble in cold water and alcohol and in acetone. It is slightly soluble in cold alcohol diluted with one-quarter its volume of water, and soluble in the same solvent when hot. It does not melt below 280°. Analysis gave 11.07 and 11.31 per cent sulfur.

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES. *Crystal habit*—Rounded grains, in part elongated and rod-like.

Refractive indices (D)— $\alpha = 1.583$, $\beta = 1.640$, $\gamma = 1.690$, $\gamma - \alpha = 0.107$, all ± 0.005; intermediate values are usually shown.

In parallel polarized light—Double refraction extremely strong, the colors being second to third order on small grains; extinction inclined, but angle not definitely determinable; elongation variable.

In convergent polarized light—Partial interference figure occasionally shown, the sign being apparently negative, and 2 E large.

Diagnostic features—The most characteristic feature of this substance is the value of the highest refractive index, γ. On immersion in a mixture of 3 parts α-monobromonaphthalene with 2 parts of methylene iodide ($n_D = 1.689$), grains so situated as to exhibit index γ will disappear in one direction or the other. Index α is also fairly distinctive, when taken in connection with the crystal habit; for the other member of this series with the same value of α, the α-1,6-compound, is markedly rod-like in habit. Aniline ($n_D = 1.585$) is an immersion liquid coming near to the value of α in refractive index, and disappearance will occur in this liquid in the case of grains lying in the proper direction.

β-NAPHTHYLAMINE NAPHTHALENE-2,6-DISULFONATE, $(C_{10}H_7NH_2)_2.C_{10}H_6(SO_3H)_2$

This salt forms a dense precipitate of microscopic plates (sometimes needle-like) which are only slightly soluble in hot solvents, and practically insoluble in the cold. It does not melt when heated to 280°. The per cents of sulfur found were 11.02 and 11.02.

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES. *Crystal habit*—Plates, with a more or less rhombic outline.

Refractive indices (D)— $\alpha = 1.610$, $\beta = 1.634$, $\gamma = 1.830$, $\gamma - \alpha = 0.220$, all ± 0.005; indices α and β are usually shown, γ appearing only on uptilted plates.

In parallel polarized light—Double refraction extreme, the colors being first to second order on very thin plates; extinction inclined at large angles, up to 40°, with respect to crystal edges often present, but parallel to the edges of uptilted plates; elongation variable on the usual plates, — on the uptilted ones.

In convergent polarized light—An interference figure frequently shown, the sign being +, and 2 E = 70° ± 5° (2 E calculated from *ns* = 76° 26′).

Diagnostic features—The habit of this substance is characteristic, and, when taken in connection with the indices as listed, renders the identification of the substance an easy matter. The lowest refractive index, α, is approximately matched by a mixture of equal parts of monobromobenzene and α-monochloronaphthalene (n_D = 1.600), and the intermediate one, β, by α-monochloronaphthalene (n_D = 1.640).

α-NAPHTHYLAMINE NAPHTHALENE-2,7-DISULFONATE, $(C_{10}H_7NH_2)_2.C_{10}H_6(SO_3H)_2$

This salt separates very slowly in the form of groups of long needles, when the hot solution is cooled. It is soluble in hot water, in hot and cold 95 per cent alcohol, and in cold alcohol diluted with one-quarter of its volume of water, but practically insoluble in cold water and in acetone. It decomposes gradually without melting when heated above 220°. It gave on analysis 11.01 and 11.24 per cent sulfur (theory 11.16).

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES. *Crystal habit*—Rods, the more slender ones slightly curved.

Refractive indices (D)— α = 1.560, β = 1.650, γ = 1.675, γ — α = 0.115, all ±0.005; index α usually shown lengthwise, and means of the others crosswise.

In parallel polarized light—Double refraction extreme, the colors being third order on even slender rods; extinction parallel; elongation —.

In convergent polarized light—Partial biaxial figure rarely shown, the sign being +.

Diagnostic features—The features most useful in identifying this substance are the value of the lowest refractive index, α, and the parallel extinction. Monochlorobenzene (n_D = 1.561) matches the index in question, and the rods disappear when their long direction lies parallel with the plane of vibration of the polarizer. Between crossed nicols the extinction is parallel, a property which distinguishes this compound sharply from the one likely to be confused with it, the 1,6-disulfonate.

β-NAPHTHYLAMINE NAPHTHALENE-2,7-DISULFONATE, $(C_{10}H_7NH_2)_2.C_{10}H_6(SO_3H)_2$

This salt forms a mass of long, slender needles on cooling a hot solution. It is soluble in hot water and 95 per cent alcohol, practically insoluble in cold water and alcohol and in acetone, and appreciably soluble in a cold mixture of 4 volumes of alcohol and 1 of water. It does not melt when heated to 280°. Analysis gave 11.07 and 11.16 per cent sulfur.

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES. *Crystal habit*—Rods, in part plate-like; sometimes showing a 130° termination; often twinned, that is, grown together in groups of two in definite crystallographic relationship.

Refractive indices (D)— α = 1.530, β = 1.700, γ = 1.740, γ — α = 0.210, all ±0.005; index α is often shown lengthwise on the twins, but crosswise on rods with parallel extinction; β is shown lengthwise on the latter.

In parallel polarized light—Double refraction extreme, colors being second or third order even on thin plates, down to first on parallel-extinguishing rods; extinction inclined, on twins making an angle of 8° ± 1° with the twinning plane, often parallel on untwinned rods; elongation variable, but usually + on untwinned rods.

In convergent polarized light—A biaxial interference figure often shown, the obtuse bisectrix being perpendicular to the plates; 2 E is evidently large and sign —.

Diagnostic features—The features most useful for identifying this substance are the habit, especially the frequent twinning; the unusually low value of the lowest refractive index, α, and the extinction relations. The lowest index is matched by methyl salicylate (n = 1.530 to 1.535); and crystals immersed in this liquid disappear in one direction or another with reference to the plane of the polarizer.

SUMMARY

The α- and β-naphthylamine salts of the naphthalene-α-, β-, 1,5-, 1,6-, 2,6- and 2,7-sulfonic acids and the ferrous salt of naphthalene-β-sulfonic acid are described. Their characteristic relative solubilities are shown in Table I and their optical properties in Table II.

TABLE I—RELATIVE SOLUBILITIES OF SUBSTANCES DESCRIBED
(Except the ferrous salt of tbe β-acid)

NOTE: d. = difficultly soluble; v. d. = very difficultly soluble; sol. = soluble; s. sol. = slightly soluble; mod. = moderately soluble; insol. = insoluble; v. s. = very sligbtly soluble.

SULFONATE	α	β	1,5	1,6	2,6	2,7
			α-NAPHTHYLAMINE SERIES			
Cold water	d.	d.	v. d.	d.	d.	d.
Hot water	sol.	s. sol.	d.	sol.	mod.	sol.
Cold 95 per cent alcohol	d.	d.	d.	s. sol.	d.	sol.
Hot 95 per cent alcohol	sol.	s. sol.	s. sol.	sol.	s. sol.	sol.
Cold 75 per cent alcohol[1]	sol.	s. sol.	d.	sol.	s. sol.	sol.
Hot 75 per cent alcohol	sol.	s. sol.	d.	sol.	s. sol.	sol.
Cold acetone	insol.	insol.	insol.	insol.	insol.	insol.
Hot acetone	insol.	insol.	insol.	insol.	insol.	insol
			β-NAPHTHYLAMINE SERIES			
Cold water	d.	v. d.	v. d.	d.	v. d.	d.
Hot water	sol.	mod.	s. sol.	sol.	s. sol.	sol.
Cold 95 per cent alcohol	d.	s. sol.	v. d.	s. sol.	v. d	d.
Hot 95 per cent alcohol	sol.	mod.	s. sol.	sol.	v. s.	sol.
Cold 75 per cent alcohol[1]	sol.	mod.	d.	sol.	d.	s. sol
Hot 75 per cent alcohol[1]	sol.	sol.	s. sol.	sol.	v. s.	sol.
Cold acetone	insol.	insol.	insol.	insol.	insol.	insol.
Hot acetone	sol.	insol.	insol.	insol.	insol.	insol.

[1] Four volumes of 95 per cent alcohol : 1 volume of water.

TABLE II—OPTICAL PROPERTIES OF SUBSTANCES DESCRIBED

	α-NAPHTHYLAMINE SERIES						FERROUS
SULFONATE	α	β	1,5	1,6	2,6	2,7	β
Habit	plates	needles	plates	rods	grains	rods	plates
Indices:							
α	1.552	1.600	1.600	1.583	1.583	1.560	1.500
β	?	1.650	?	1.730	1.640	1.650	?
γ	1.799	1.725	1.795	1.770	1.690	1.675	1.660
γ — α	0.243	0.125	0.195	0.187	0.107	0.115	0.160
Usual	α & γ	γ	α & γ	α & γ	meaos	α	α & γ
Colors	1–2	1	2	2–3	2–3	3	2
Extinction	par.	par.	incl.	17°	incl.	par.	par.
Elongation	indet.	+	indet.	—	indet.	—	indet.
Figure	0	0	rare	occas.	occas.	rare	occas.
2 E	indet.	indet.	indet.	large	large	indet.	large
Sign	indet.	+	indet.	—	—	+	+

	β-NAPHTHYLAMINE SERIES						β-Acid Salt
SULFONATE	α	β	1,5	1,6	2,6	2,7	1,5
Habit	plates	plates	plates	needles	plates	rods	plates
Indices:							
α	1.620	1.640	1.631	1.550	1.610	1.530	1.550
β	1.670	?	1.647	1.700	1.634	1.700	1.700
γ	1.850+	1.730	1.755	1.755	1.830	1.740	1.850+
γ — α	0.230+	0.090	0.124	0.205	0.220	0.210	0.300+
Usual	α & β	α	α & β	α	α & β	α	α & β
Colors	1–2	1–2	1	3–4	1–2	2–3	3–4
Extinction	par.	indet.	indet.	par.	40°	8°	indet.
Elongation	+	indet.	indet.	—	±	±	indet.
Figure	usual	rare	usual	occas.	usual	usual	occas.
2 E	85°	indet.	75°	large	70°	large	large
Sign	+	indet.	+	—	+	—	+

NAPHTHALENE SULFONIC ACIDS. II—A METHOD FOR THE QUALITATIVE DETECTION OF SOME OF THE NAPHTHALENE SULFONIC ACIDS[1]

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During the course of experiments on the sulfonation of naphthalene it became desirable to have a fairly rapid and convenient way of detecting the presence of the various sulfonic acids formed when naphthalene is subjected to the action of sulfuric acid under varying conditions. No readily applicable method is to be found in the literature. The identification has always been made by means of the chlorides or amides, which is unsatisfactory for rapid work when dealing with mixtures of two or more of the acids. The technical separations are effected by means of the different solubilities of their calcium or sodium salts, but this method is not adapted to making a qualitative differentiation, for example, of naphthalene-1,6-sulfonic acid from the isomeric 2,7-sulfonic acid, or of naphthalene-β-sulfonic acid from the 2,6-disulfonic acid, since the solubilities of the salts of these pairs of acids are similar.

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[1] Presented at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

The use of the salts of these acids with organic bases for qualitative separations was not described by Erdmann and Süvern[1] who studied the solubilities of the aniline, benzidine, and *o*-tolidine salts of the α-, β-, 2,6- and 2,7-sulfonic acids of naphthalene. They state that these salts are very valuable for the isolation of the easily soluble sulfonic acids. Their observation that the aniline salts of the α- and 2,7-acids are soluble in cold water, while the corresponding salts of the β- and 2,6-acids are insoluble, suggested the possibility that salts with other organic bases may have properties suitable for a qualitative distinction of the acids. Accordingly, a large number of such salts were prepared and their properties studied. The most important of these salts have been described in the preceding article, and from an examination of their properties the following method of analysis has been developed. Before attempting this method, the chemist should make and become familiar with the salts described in the preceding article or at least with those which are used in this analytical method. If this is done, he will have very little difficulty in distinguishing the various acids by this method.

ANALYTICAL METHOD

REAGENTS—(1) A freshly prepared solution of ferrous chloride.

(2) A hot saturated solution of α-naphthylamine hydrochloride made fresh just before use by dissolving the free base in hot dilute hydrochloric acid.

(3) A standard normal solution of sodium hydroxide.

(4) A hot saturated solution of β-naphthylamine hydrochloride.

(5) Acetone.

(6) Methyl salicylate (oil of wintergreen or birch).

(7) Microscope fitted with two nicol prisms and a revolving stage.

PREPARATION OF SOLUTION—The sodium salts of the sulfonic acids are prepared free from sulfates by the usual method of treating the sulfonation mass with lime, filtering from calcium sulfate, and treating the calcium salts in solution with sodium carbonate. The solution is then filtered to remove calcium carbonate, and the filtrate is acidified slightly with hydrochloric acid.

The solution may be of any convenient strength. Twenty-five cc. of a 5 per cent solution are in most cases ample for a complete analysis.

QUANTITIES USED—The tests may all be made on small quantities in test tubes; for example, 2 cc. of solution or a few milligrams of solid, unless otherwise stated in the directions. Also, except when removing an acid from the solution, 2 or 3 cc. of the reagent employed are adequate, except as noted below.

TEST FOR NAPHTHALENE-β-SULFONIC ACID

Ferrous chloride added to the cold solution produces a precipitate of glistening micaceous flakes of ferrous naphthalene-β-sulfonate.[1] This may be slow in forming if the amount is small.

If this acid is detected, it is removed from the entire solution by adding a slight excess of ferrous chloride and filtering off the iron salt precipitated. The filtrate is then concentrated to its original volume before making the following test.

TEST FOR NAPHTHALENE-1,5-DISULFONIC ACID

To a portion of the filtrate, heated to boiling, is added an excess of boiling α-naphthylamine hydrochloride solution, and the solution boiled down to its original volume. A granular precipitate of α-naphthylamine naphthalene-1,5-disulfonate,[1] formed while concentrating, indicates the presence of the acid.

Difficulty is sometimes encountered here in causing the insoluble salt to precipitate. If, however, the α-naphthylamine hydrochloride solution is made directly before using, by dissolving the free base in hot dilute hydrochloric acid (decolorizing with norit or bone-black when necessary), and employing a large excess of this reagent, there is no difficulty in obtaining a reaction. The explanation of the fact that a solution freshly prepared from the base is more efficacious than one made, for example, by dissolving the dry hydrochloride of the base in water, or than a solution which has stood for some time, is not known.

In adding this solution, an excess over that required to combine with all the sulfonic acids present must be used, as otherwise the insoluble salt does not form. A possible explanation of this fact may be that the disulfonic acid may form a soluble acid salt with α-naphthylamine.

If 1,5-acid is found, it must be removed from the rest of the solution before making any subsequent tests. To the boiling solution an excess of a boiling solution of the base is added, the mixture is concentrated to its original volume and filtered hot. The excess of the base is then removed from the filtrate by titrating to alkalinity with sodium hydroxide, using phenolphthalein for indicator. After cooling, the free base is removed on a filter, and the filtrate acidified with hydrochloric acid.

TEST FOR NAPHTHALENE-2,6-DISULFONIC ACID

The entire solution which has been freed from both β- and 1,5-acids is heated to boiling, and a large excess of boiling β-naphthylamine hydrochloride solution is added. The amount used must be sufficient to form neutral salts with all sulfonic acids present.

The 2,6-acid is indicated by a white precipitate of β-naphthylamine naphthalene-2,6-disulfonate[2] formed while boiling. The solution is filtered rapidly while hot, and the filtrate allowed to cool.

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[1] *Ann.*, **275** (1893), 297.

[1] See p. 1083 of preceding paper.

[2] See p. 1084 of preceding paper.

The formation of a crystalline precipitate in the filtrate on cooling does not necessarily indicate the presence of any of the remaining acids, since the β-naphthylamine naphthalene-2,6-disulfonate is not completely insoluble in hot water. However, the presence of other naphthalene sulfonic acids at this point has a salting-out effect on the 2,6-salt, and hence its precipitation is more complete in hot water when some of the naphthalene sulfonic acids are present whose β-naphthylamine salts are soluble in boiling water (the α-, 1,6- or 2,7-acids). When none of these acids are present, the salt separating on cooling is distinctive—white, fine, and voluminous—and when once seen would never be mistaken for the salts of any of the other naphthalene sulfonic acids not yet removed.

TEST FOR NAPHTHALENE-α-SULFONIC ACID

The filtrate from the previous test is allowed to cool and stand at least one hour after it is cold to insure complete crystallization of the difficultly soluble salts. Should a jelly be formed, more water is added, and the solution heated to boiling and cooled again. The salts are then filtered and dried in a vacuum oven at 100° C. The filtrate should be tested with more of the cold reagent to be sure of complete precipitation.

A small quantity of the dry salts is boiled with 2 or 3 cc. of acetone, filtered through a warm, dry funnel, and the filtrate cooled. The presence of α-sulfonic acid is shown in the cold filtrate by the separation of crystals of β-naphthylamine naphthalene-α-sulfonate.[1]

If this acid is found, the whole mass of the salts is boiled with acetone, filtered hot through a warm, dry funnel, boiled again with acetone, filtered, and the residue washed with hot acetone. The insoluble salts are then dried and examined under the microscope.

OPTICAL PROPERTIES—Immerse the salts in methyl salicylate or other oily liquid having a refractive index near 1.53. Turn the stage to bring a clear-cut crystal (rod or plate) into parallelism with the plane of vibration of the polarizing nicol prism (as indicated by one of the cross hairs; which cross hair must be determined in advance).

If the crystal boundaries disappear, indicating the identity of refractive index of the liquid with that of the crystal in the direction of elongation; and if, on inserting the analyzing nicol, in crossed position, the extinction is more or less inclined, *i. e.*, if the crystal becomes dark when turned so as to make an angle of up to nearly 10° with a cross hair, the presence of naphthalene-2,7-disulfonic acid as its β-naphthylamine salt is indicated. This salt of the 2,7-acid also shows a characteristic twinning habit, the two parts of the crystal plates showing extinction in different positions. These twinned plates also show an approximately 120° termination.

If the crystal boundaries remain distinct, and, on raising the microscope tube, a band of light appears to enter the crystal, showing that its refractive index exceeds that of the liquid in the direction of elongation; and if, on inserting the analyzing nicol in crossed position, the extinction is parallel, *i. e.*, the crystal becomes dark when parallel to a cross hair, the presence of naphthalene-1,6-disulfonic acid also as the β-naphthylamine salt is indicated. If salts of both acids are present, both behaviors can be readily recognized on separate crystals.

These optical properties are very characteristic of these two salts, as may be seen by referring to the table of optical properties given in the preceding article. The very small amounts of the salts of any of the other four naphthalene sulfonic acids which may be present at this point of the analysis do not in any way interfere with these observations, and are readily recognized as impurities.

DELICACY OF THE TESTS

Most of the above-described tests are as delicate as it is necessary for them to be when used for technical purposes.

The precipitation of the β- and 2,6-acids is very nearly quantitative, so that a rough estimate of the amounts of these present can be made by weighing the dried precipitates. The precipitation of the 1,5-acid is not so complete, since α-naphthylamine naphthalene-1,5-sulfonate is slightly soluble in boiling water. The α-sulfonic acid salt is almost completely insoluble in cold water, and by evaporating the acetone extract, its weight may be obtained, since none of the other salts are appreciably soluble in acetone. A rough estimate of the relative amounts of the 2,7- and 1,6-salts may be made under the microscope.[1]

SUMMARY

A method is proposed for the qualitative examination of mixtures of the following naphthalene sulfonic acids: α- and β-monosulfonic, and 1,5-, 1,6-, 2,6-, and 2,7-disulfonic acids.

THE MECHANISM OF BATING[2]

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Perhaps the most curious of all the processes involved in making leather is that of bating. Little is known of its origin because it was a secret process, but it is at least some centuries old. After the skins are taken from the lime liquors, unhaired, and washed, they are plump and rubbery, a condition not particularly suitable for putting them directly into the tan liquors. The object of bating is to prepare the unhaired skins for tanning, and originally consisted in keeping them in a warm infusion of the dung of dogs or fowls until all plumpness had disappeared and the skins had become so soft as to retain the impression of thumb and finger when pinched and sufficiently

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[1] See p. 1082 of preceding paper.

[1] The authors wish to extend their thanks to Messrs. G. O. Oberhelman and D. F. J. Lynch for their kindness in checking and confirming this method, and for suggestions they have made for its improvement.

[2] Presented before the Section of Leather Chemistry at the 60th Meeting of the American Chemical Society, Chicago, Ill., Sept. 6 to 10, 1920.

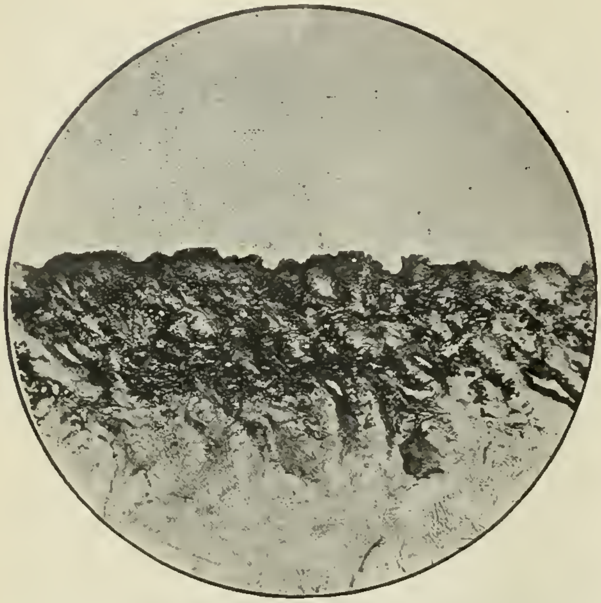

Fig. 1—Cross Section of Grain and Papillary Layer of Calfskin Bated without Trypsin. Note Elastin Fibers in Upper Half. Magnification 42 ×

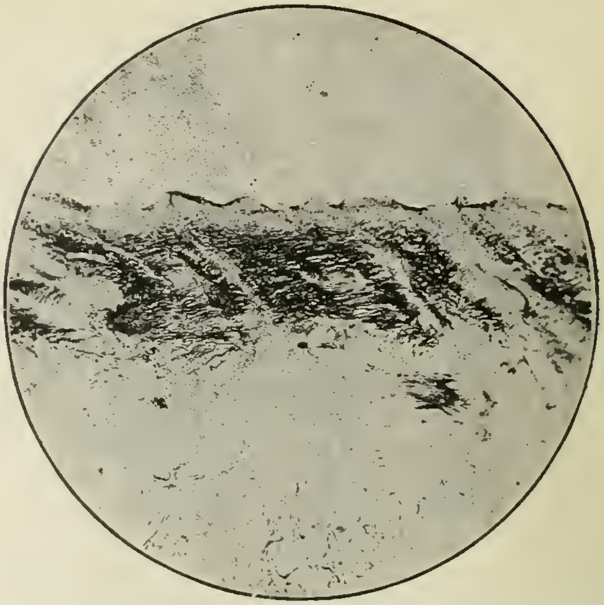

Fig. 2—Cross Section of Grain and Papillary Layer of Calfskin Bated for 6 Hrs. with Trypsin. Elastin Fibers Partly Removed. Magnification 42 ×

porous to permit the passage of air under slight pressure. In his book Wood[1] says:

> The object of bating or puering is to render the skins, and the resulting leather, soft and supple. * * * Puering is not only a filthy and disgusting operation, but is prejudicial to health and in the nature of it is attended by more worry and trouble than all the rest of the processes in leather making put together.

Wood made a thorough study of dungs and their action upon skins and his final opinion was that the active constituents of the dung infusions were ammonium compounds and pancreatic or similar enzymes. As a result of this work, and some practical development by others, dung has been replaced as a bating material in many tanneries by a mixture of ammonium chloride and pancreatin.

Our knowledge of the behavior of proteins in contact with aqueous solutions of acids, bases, and salts, in which the protein swells by absorption of water to an extent depending upon the nature and concentration of the electrolyte, raises the question as to whether bating is not simply a means of bringing the skins into a condition of minimum swelling, especially since such a condition would give the skins those physical properties which are widely accepted as indicative of properly bated skins. If this were so it would reduce bating to perhaps the simplest of the tannery processes.

EXPERIMENTAL

The following experiment was made to show the comparative degrees of swelling of hide in lime water, in a bate liquor, and in water. In each of three 100 cc. graduated cylinders were placed 2 g. of "Standard" hide powder. The first was filled with saturated lime water, the second with distilled water, and the third with a bate liquor showing a value for log H^+ of —8.1. The cylinders were stoppered and shaken at intervals, and the swollen powders allowed to settle. At the end of 8 hrs. the volumes occupied by the powders were as follows: in lime water 41 cc., in distilled water 32 cc., and in the bate liquor 31 cc., showing that the bate liquor actually causes less swelling of hide than ordinary distilled water. A pure solution of ammonium chloride of the same concentration and alkalinity as the bate liquor produces practically the same degree of swelling.

A more practical test was made by comparing the action of ammonium chloride alone with that of a commercial bate, supposedly containing ammonium chloride and pancreatin. Both liquors were made up to a concentration of 1.20 g. of ammonium chloride per liter, skins of similar nature were put into each, and all other conditions kept as nearly alike as possible. At the end of several hours the skins in both liquors had all the physical properties of bated skins and no difference between the two lots could be detected, even after tanning. Recently a number of chemists in various parts of the country have informed the author of similar findings. This test would seem to indicate one of two things—either that pancreatin was of no practical benefit, or else that the commercial bate was deficient in enzymes.

Some years ago Rosenthal[1] concluded that the bating process removes elastin from the skin. In a sample from the butt of a calfskin he found 10.36 per cent of elastin, calculated on the dry basis, before bating, and only 0.31 per cent after bating. But, as a measure of the elastin content of a skin, he used the per cent of nitrogenous matter that could be rendered soluble by tryptic digestion, whereas his bating process was also supposedly a tryptic digestion. What he proved was merely that bating removed almost to completion certain nitrogenous matter from the limed skin, but whether this was elastin or hide substance

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[1] "Puering, Bating and Drenching of Skins," Spon, **1912**.

[1] *J. Am. Leather Chem. Assoc.*, **11** (1916), 463.

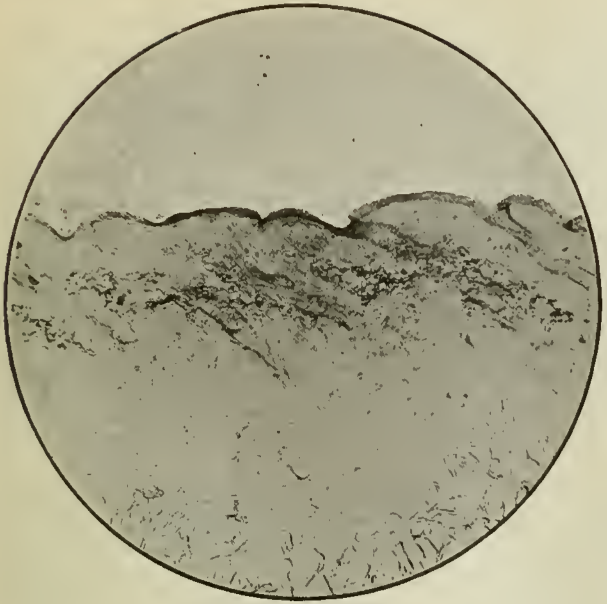

Fig. 3—Cross Section of Grain and Papillary Layer of Calfskin Bated for 20 Hrs. with Trypsin. Few Elastin Fibers Left. Magnification 42 ×

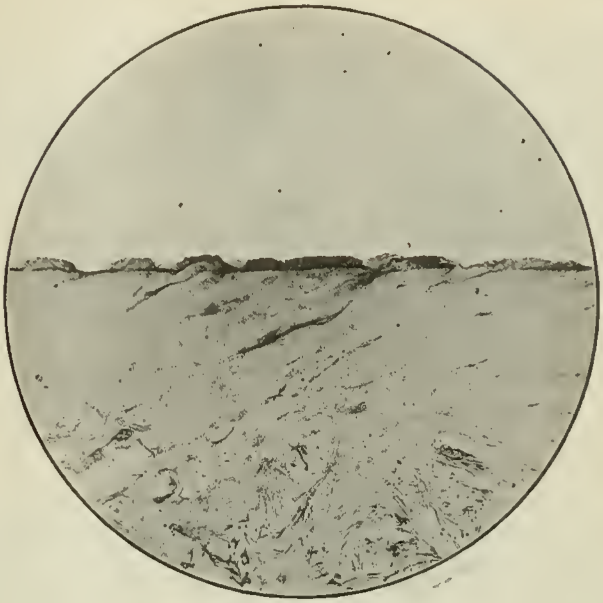

Fig. 4—Cross Section of Grain and Papillary Layer of Calfskin Bated for 24 Hrs. with Trypsin. Elastin Fibers Entirely Removed. Magnification 42 ×

which had previously been attacked by lime appears open to question.

The statement that elastin is removed by bating is also made by Moeller[1] and by Seymour-Jones,[2] who in collaboration with Wood carried out an interesting experiment on the bating of sheepskin. The "flywing" grain of a sheepskin was split from the main body of the skin, called simply flesh for convenience, and both grain and flesh were cut into halves along the backbone. One grain and one flesh were bated with pancreatin, while the other halves were delimed with acetic acid, but not bated. All four pieces were then tanned with sumac. There was comparatively little difference between the bated and unbated flesh halves, but the grain samples were very different from each other. The bated grain was soft and even, with the hair-holes clean and clear, but in the unbated grain the hair-holes appeared to be glued up and the surface had a rough, contracted appearance. Seymour-Jones concluded that elastin is present only in the grain membrane and that it must be digested before tanning to produce a satisfactory grain, but that bating of the skin under the grain is not only unnecessary, but often undesirable.

The results of this experiment may, however, not have been due to the bating process since one grain had been treated with acetic acid, while the other apparently had not. The author recalls having tanned in the same liquor a bated skin and one both bated and pickled. The difference between the tanned skins was striking, the pickled skin being shriveled to half of its original area and having an almost corrugated appearance, while the other had not shrunk at all and was quite smooth.

It was decided to settle definitely the question of the removal of elastin in the bating process by means of photomicrographs of cross sections of the skins taken before and after bating. The elastin fibers are not clearly discernible unless suitably stained, and for this purpose magenta has been found excellent, since it makes the elastin much darker in color, and therefore more prominent than the rest of the skin. Two liquors were prepared, each containing 1.20 g. per liter of ammonium chloride, while one also contained 0.03 g. per liter of a U. S. P. grade of trypsin. Enough alkali was added to each to make the value for log H^+ about —8.0. A piece of limed calfskin was kept in each of these liquors for 24 hrs. at about 37°. Microscopic examination of the sample from the trypsin liquor showed that practically all of the elastin had been removed, while, in the piece treated with ammonium chloride only, the elastin was left apparently unaltered. The test was carried out on a large scale with the same result.

The time factor in the removal of elastin can be followed by means of the photomicrographs shown in Figs. 1 to 4, inclusive.[1] The sections, which are all 40μ thick, have been stained with magenta to make the elastin fibers more prominent. In Fig. 4 the grain membrane shows clearly enough to be measured, and is about 0.046 mm. thick. The skins are from medium-size calves, and all sections shown were taken from the butt. In a section 2.5 mm. thick the elastin fibers were present to a depth of 0.5 mm. from the grain surface, then for a distance of 1.7 mm. no elastin could be detected, but was abundant in the remaining 0.3 mm. of flesh surface. This fully confirms the view of Seymour-Jones that the main body of skin contains no elastin.

The value of removing elastin from skins must depend to some extent upon the particular properties desired in the leather, but between skins containing elastin and those from which it had been removed no such differences as were noted by Seymour-Jones could be detected, probably because the differences he found were due to causes other than bating.

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[1] *Collegium*, **1918**, 105, 125; *Chem. Abs.*, **12** (1918), 2706.

[2] *J. Soc. Leather Trades' Chem.*, **4** (1920), 60.

[1] Acknowledgment is made of the assistance of Mr. Guido Daub in the preparation of the photomicrographs.

CONCLUSION

The mechanism of bating evidently consists of two distinct parts: (1) Reducing limed skins to a condition of minimum swelling; (2) digesting the elastin fibers present in the outer layers of the skins.

INCLUSIONS AND FERRITE CRYSTALLIZATION IN STEEL. II—SOLUBILITY OF INCLUSIONS[1]

By E. G. Mahin and E. H. Hartwig

Department of Chemistry, Purdue University, Lafayette, Indiana

In an earlier paper by one of us[2] experimental evidence was offered for the widely held theory that nonmetallic inclusions are partly responsible for ferrite segregation in steel, indicating that Stead's view to the contrary[3] may be incorrect. Stead had concluded, as a result of his experiments, that phosphorus segregation about inclusions is responsible for this phenomenon, and that the presence of inclusions has no direct bearing upon ferrite formation from slowly cooled hypoeutectoid steels. The writer, on the other hand, showed that ferrite continues to segregate about inclusions even after long heating at temperatures considerably above Ar_3, although the longitudinal ferrite streaks of rolled steel disappear because of the better dissemination of phosphorus that is brought about by such heating.

To account for this definitely established fact, it was assumed that either the material of the inclusion itself or some reaction product of this with surrounding metal (or both of these) is soluble, to a slight extent at least, in iron or in austenite, and that the presence of this dissolved material so alters solubility relations as to cause the beginning of ferrite separation from austenite in the regions so penetrated, before supersaturation has broken down at other points.

The mechanism of the breakdown of the solid solution of hypoeutectoid steel is somewhat as follows:

As the steel cools slowly through the transformation range, the austenite of higher temperatures becomes saturated with ferrite at the ideal temperature, A_3. Ferrite does not, in any case, separate at this point, but remains in solution until a somewhat lower temperature, Ar_3, is reached, when the supersaturation then existing can no longer be maintained. When ferrite separation begins, recalescence occurs, and austenite continues to reject ferrite about the crystal nuclei thus formed until the temperature has fallen to Ar_1, when austenite of eutectoid composition remains and is changed bodily to pearlite.

However, it is not to be supposed that the *degree* of supersaturation of ferrite in austenite is the same in all parts of the steel mass, or even in all parts of a given austenite grain. Austenite of absolutely uniform concentration is an ideal substance, probably never existing in a given steel mass. Even if all elements but carbon and iron could be excluded, such uniformity could be approached only in steel cooling from the liquid state, because when a cooled hypoeutectoid steel is reheated, reabsorption of ferrite by austenite, as the transformation range is traversed, gives austenite grains containing more iron carbide toward their centers and more iron in the outer portions and, while diffusion is a fairly rapid process, it is not likely that any ordinary heating entirely serves to correct this lack of uniformity in concentration. It is therefore in the regions of higher iron concentration that supersaturation during cooling is greatest and, leaving other influences out of account, it is in these regions that the nuclei of ferrite grains are first generated.

It is a general condition that if a third substance is added to a binary solution which is already saturated with one of its components, the solubility of this component is lowered. The opposite is sometimes true, and in certain cases of ordinary solutions the presence of the third substance has little observable effect, but these cases are exceptional. In the binary solid solution, iron–iron carbide, the nonmetallic inclusion or a reaction product may be regarded as the third substance. It is not necessary to assume a large solubility for this third substance. If there is a zone, however narrow, lying about an inclusion and containing even a trace of some third dissolved substance derived from the inclusion itself, the presence of this material should alter the solubility of ferrite in the austenite there present, and thus cause local breakdown of the cooling solution first in these regions. This would establish ferrite nuclei, and separation would continue at these points. The cooled steel would then show inclusions embedded in ferrite.

One reaction product was suggested in the first paper. This was manganese, an equilibrium product resulting from contact of manganese sulfide inclusions with iron. It would appear that the steel in contact with such an inclusion must necessarily contain manganese in slightly higher concentration than in other regions. This would also be true of manganese sulfide itself and of ferrous sulfide existing in equilibrium with the other substances involved in the reaction.

Similar reactions are conceivable in the case of oxides, silicates, sulfides, etc., of elements other than iron, and the reaction products, as well as the original inclusions, must dissolve to a slight extent in the surrounding metal.

It was earlier pointed out that the effort to produce artificial inclusions by sealing powders into holes in steel could not be expected to produce any very definite results, because air could not be entirely excluded from such cavities, and the film of oxide produced on the lining of the cavity when the steel was heated must prevent intimate contact with the inclusion, even if the latter were fusible. Of nine materials used by Dr. Stead, at least five (calcium fluoride, calcium oxide, magnesium oxide, silica, and manganese sulfide) would be infusible, or practically so, at 1000° C., the temperature employed.

The difficulties attending the production of intimate contact of artificial nonmetallic inclusions with surrounding metal are not encountered if metallic inclusions are used. Clean holes may be drilled in the steel, and clean, tightly fitting rods of a different material

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[1] Read at the 59th Meeting of the American Chemical Society St. Louis, Mo., April 12 to 16, 1920.

[2] Mahin, This Journal, 11 (1919), 739.

[3] *J. Iron and Steel Inst.*, 97 (1918), 287, 389.

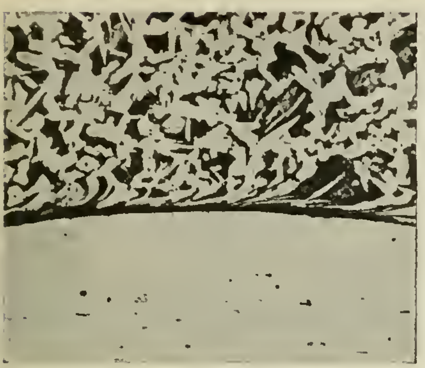

Fig. 1—Aluminium Bronze (Below) in Steel. Not Heat Treated. × 100

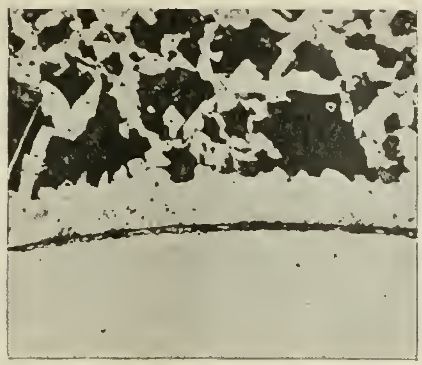

Fig. 2—Aluminium Bronze in Steel. Heat Treated. × 100

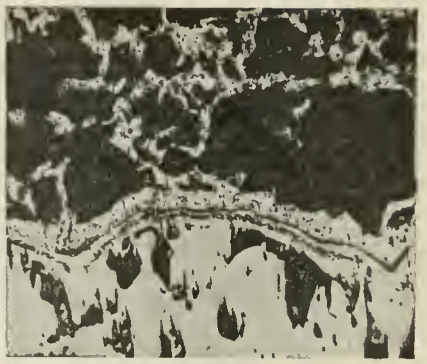

Fig. 3—Zinc-Aluminium Alloy in Steel. × 100

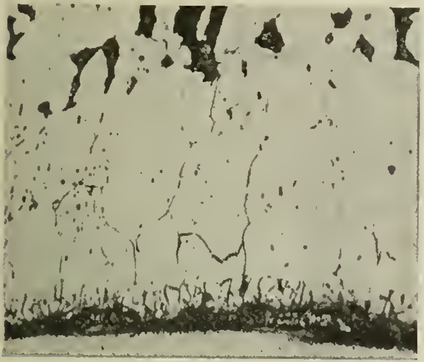

Fig. 4—Stellite in Steel. × 100

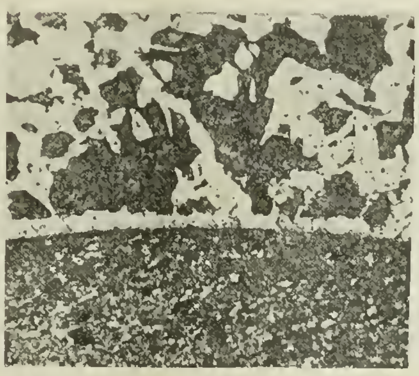

Fig. 5—High-Speed Steel in Carbon Steel. × 100

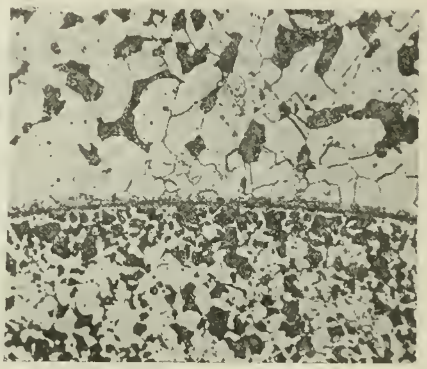

Fig. 6—Steel (Mn 1.74%) in Steel (Mn 0.67%). × 100

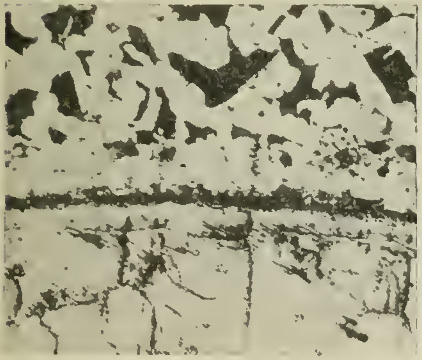

Fig. 7—Illium in Carbon Steel. × 100

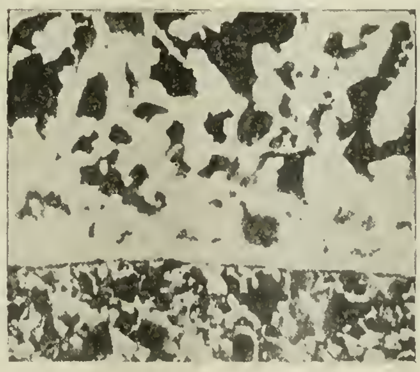

Fig. 8—Steel (Cr 1.0%) in Carbon Steel. × 100

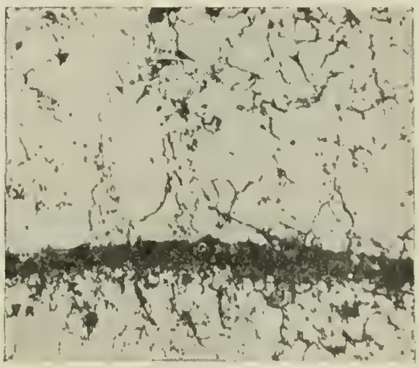

Fig. 9—Steel (Ni 3.5%) in Carbon Steel. × 100

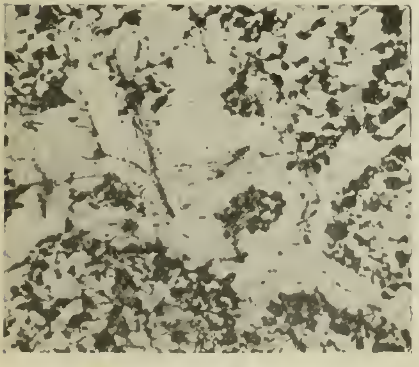

Fig. 10—Titanium Steel with Segregated Ferrite. × 100

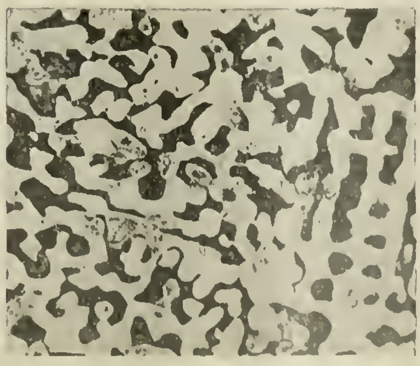

Fig. 11—Steel (Si 4.0%). × 50

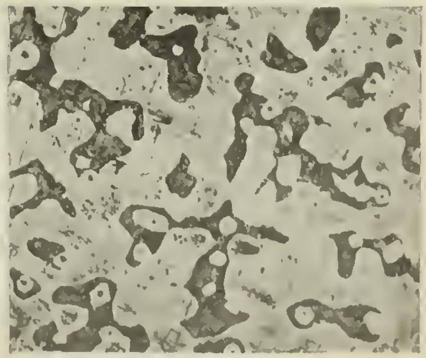

Fig. 12—Steel (P 1.06%) × 50

driven into the cold. unoxidized steel. In this way it is possible to use nonferrous metals, alloys, or alloy steels to determine the effect of a third metal or combination of metals, thus imitating the production of a metal by reaction of a nonmetallic inclusion with surrounding steel. This was the idea which prompted the work described below. From the success attained the work was extended to include an investigation of the broader question as to the effect of segregation of such substances as silicides, sulfides, and phosphides, and of metallic elements of alloy steels, upon carbon distribution.

EXPERIMENTAL PART

A bar of rolled carbon steel, containing 0.53 per cent carbon, was cut transversely into plates about one inch in thickness. Through these were drilled holes one-eighth inch in diameter, no oil or cutting compound being used. Rods of a number of alloys, carefully turned to 0.002 in. oversize, were driven into these holes. The ends of such as were sufficiently malleable were riveted down. The piece of steel, with its insert, was then placed in a closed muffle furnace and heated to 850° C. (which was well above the transformation range for this steel) for periods of 7 hrs. After cooling in the furnace the pieces were sectioned transversely to the axis of the insert, polished, and etched in nitric acid. Microscopic examination of the polished sections was made before etching, to determine whether contact of the pieces had been perfect. In the few cases where the insert had not been fitted tightly the specimens were rejected. Of the others, photomicrographs were made for record.

The following alloys and steels were used as inserts in the first series of experiments: Aluminium bronze (copper 90, aluminium 7, iron 3), stellite, die-casting alloy (zinc and aluminium), high-speed steel, and steel containing 1.74 per cent manganese.

The results of the treatment are shown in the accompanying photomicrographs, in each of which the steel and the insert are shown in the upper and lower portions, respectively. A well-defined ferrite ring surrounding the insert is evident in all cases. (In all of the photomicrographs there is a narrow, dark line, somewhat indistinct in some cases, at the contact circle separating steel and insert. This is due to the fact that there is usually a difference in hardness of the steel and insert, so that polishing produces a rounded shoulder at the contact surface. With vertical illumination this appears as a dark ring.)

ALUMINIUM BRONZE—Fig. 1 shows the appearance of the contact line between steel and aluminium bronze insert before thermal treatment. The other experimental pieces were similar to this in appearance. The contact is excellent, the only change in grain structure being a physical distortion of grains adjoining the insert, this being produced by driving in the cold insert. Fig. 2 shows the same piece after 7 hrs. heating at 850° C. A ferrite ring, clearly defined and uniform in width, entirely surrounds the insert. The obvious assumption is that outward diffusion of the foreign metal, dissolving in contiguous austenite, lowers ferrite solubility and causes separation first in the zone penetrated.

ZINC-ALUMINIUM—The die-casting alloy was heated above its fusing point, and the line representing the contact surface of the cavity and melted metal has become irregular. However, the ferrite ring, not so wide in this case, follows this outline, as shown in Fig. 3.

STELLITE—In Fig. 4 is shown the very striking effect of a stellite insert. Either cobalt or chromium appears to diffuse quite rapidly into steel and to exert a considerable effect upon ferrite solubility. Possibly both metals are responsible for this effect. The ferrite ring here produced is the widest of all that were obtained in the experiments described in this paper, with the exception of that produced by manganese and nickel, to be discussed later.

CHROMIUM-TUNGSTEN—The action of a high-speed steel insert is illustrated in Fig. 5. The ferrite ring is narrow, but regular in width, and very distinct.

MANGANESE—The action shown in Fig. 6 is interesting. Here the insert and the steel body are of practically identical composition except with regard to manganese, the insert containing 1.74 per cent of this element as against 0.67 per cent in the outer body. Above the transformation range, manganese has diffused outward from the region of greater concentration into that of lower concentration. Ferrite solubility has apparently been diminished in the outer piece and, as might have been predicted, somewhat increased in the outer border of the insert. Consequently, a ring of increased pearlite concentration is observed in the last-mentioned zone. (A still wider ferrite ring, produced by manganese diffusion, is shown in Fig. 17.)

ILLIUM—Illium metal (chromium-nickel-copper) produces a narrow ferrite ring when the specimen is heated for 9 hrs. at 850° C. This is shown in Fig. 7.

CHROMIUM AND NICKEL—A chrome steel (chromium 1.0 per cent) shows a well-characterized effect (Fig. 8), and a nickel steel (nickel 3.5 per cent) produces a wide ferrite band, as shown in Fig. 9.

In the experiments just described the materials used as pseudo-inclusions consisted of alloys and steels that happened to be available, and they were used in this way to test the general effect of localizing metallic impurities. In the further attempt to use inserts made from miscellaneous steels, each high in some single element, it was soon found that the results of the heat treatment were complicated by differences existing between the insert and body, with respect to the per cents of carbon, as well as of the common elements, silicon, phosphorus, sulfur, and manganese.

The National Malleable Castings Co., through the courtesy of Mr. H. A. Schwartz, chief metallurgist, kindly undertook to prepare a set of special steels that would be better adapted to this use. One stock steel was made, containing 0.5 per cent of carbon and normal per cents of the four other common elements. To various other portions of this same steel abnormally high amounts of special elements were added in the crucible. These special steels were used as in-

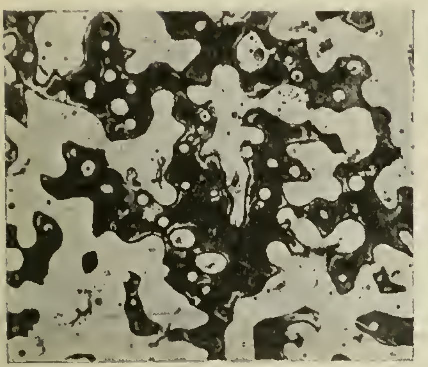
Fig. 13—Same Steel as in Fig. 12 Copper Reagent. × 50

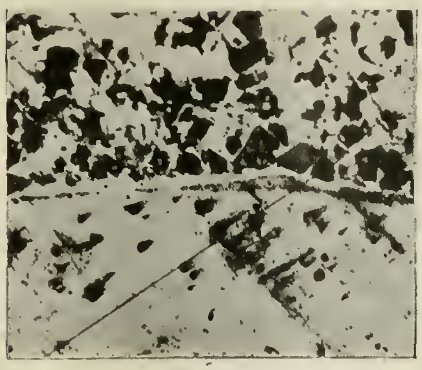
Fig. 14—Same Steel (Below) as in Fig. 12 in Carbon Steel. × 100

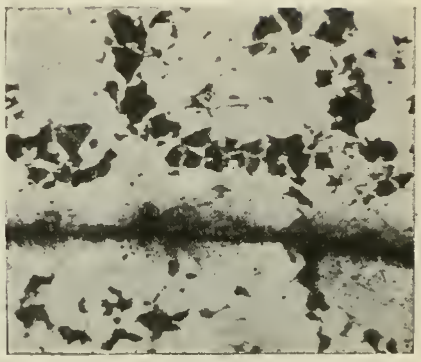
Fig. 15—Steel (S 1.36%) in Carbon Steel. × 100

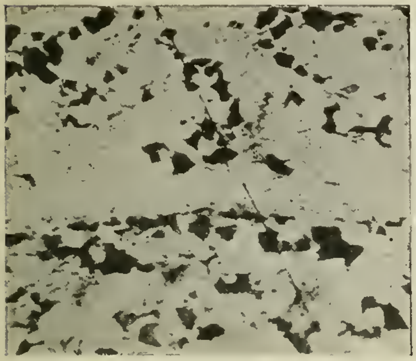
Fig. 16—Steel (Cu 1.34%) in Carbon Steel. × 100

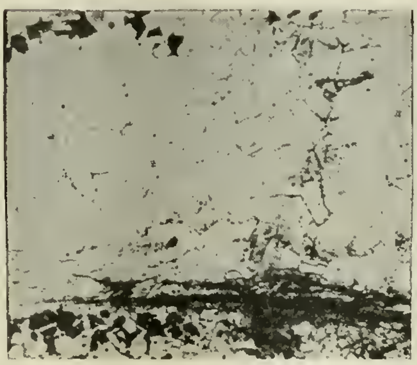
Fig. 17—Steel (Mn 1.46%) in Carbon Steel. × 100

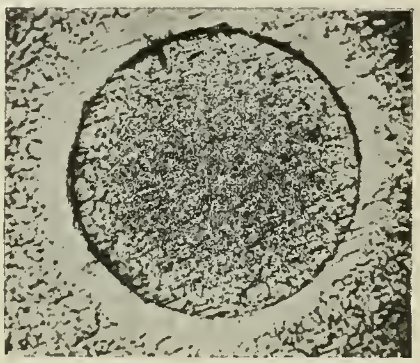
Fig. 18—Same as in Fig. 17. × 12

serts in the stock for heat treatments similar to those described in the first part of this paper. The following per cents of the special elements were found by analysis: Phosphorus 1.06, sulfur 1.36, silicon 4.0, manganese 1.46, chromium 0.84, and copper 1.34. A special titanium steel also was available, but the experiments upon this are still incomplete. Some further work upon all of these specimens is still in progress, but it may be of interest to dwell briefly upon the effects of some of the special elements upon carbon distribution.

The method used for making the special steels was, as noted above, the addition of ferromanganese, ferrosilicon, and ferrotitanium, as well as of steels containing high proportions of iron phosphide, iron sulfide or chromium, to a crucible containing fused carbon steel. The carbon was thus maintained practically constant, but under the conditions it could scarcely be expected that the special steels would be uniform in composition, with respect to the special element added. This lack of uniformity in the special steel insert gives two interesting results:

(1) The ferrite ring produced in the carbon steel surrounding the insert varies greatly in width, presumably according to the variation in concentration of the special element along the cylindrical surface of the insert.

(2) The special steel itself shows pronounced carbon segregation.

The latter point is illustrated by Figs. 10, 11, and 12, photomicrographs of the annealed titanium, silicon and phosphorus steels, respectively. The segregated masses of ferrite grains probably contain a higher proportion of the special element than other parts of the metal. This is proved to be the case, at least with the phosphorus steel, by a comparison of Figs. 12 and 13, the latter being a representation of this special steel attacked by Stead's copper reagent. The bright high-phosphorus areas, free from copper, correspond well with the ferrite grains of Fig. 12.

PHOSPHORUS—It has already been noted by Stead, and confirmed by the work reported in a previous paper by one of the present writers,[1] that iron phosphide migrates very slowly in austenite. It is interesting to notice that the insert of steel containing 1.06 per cent of phosphorus, when heated to 850° C. for 4 hrs., produces only a very narrow (and somewhat irregular) ferrite ring in the steel surrounding the insert (Fig. 14). It is planned to give this specimen a protracted heat treatment at a higher temperature in order to observe whether the effect will be more pronounced.

SULFUR—The effect of sulfur, through migration of ferrous sulfide, is shown in Fig. 15. The contact line is somewhat obscured, in this view, on account of the smearing that occurs during the polishing action upon the somewhat brittle material.

COPPER—Copper migrates readily and affects carbon distribution, as do the other elements noted (see Fig. 16).

MANGANESE—Manganese shows a more pronounced effect than does any other of the common elements

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[1] *Loc. cit.*

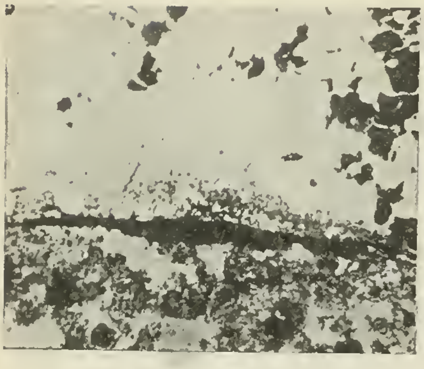

Fig. 19—Steel (Si 4.0%) in Carbon Steel. × 100

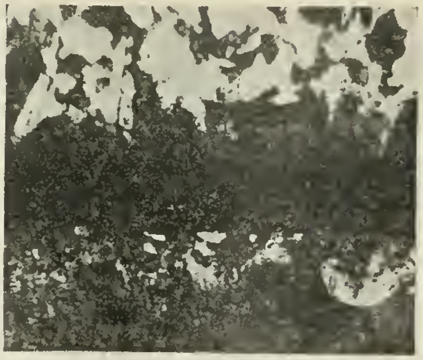

Fig. 20—Brass in Carbon Steel. Air Pocket. × 100

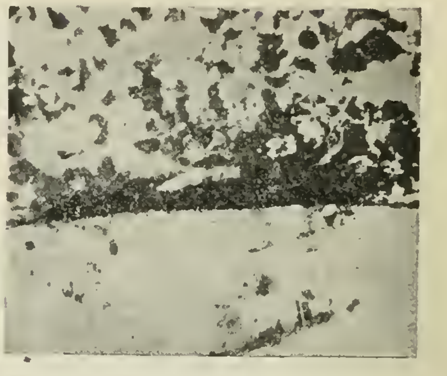

Fig. 21—Steel (P 1.06%) in Carbon Steel. Air Pocket. × 100

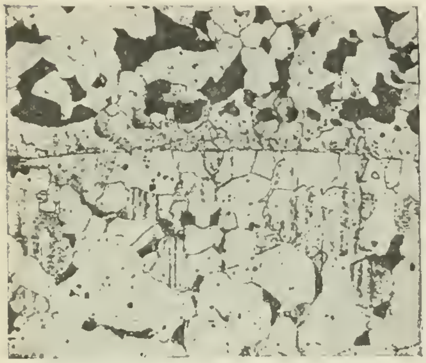

Fig. 22—Ingot Iron in Carbon Steel, Showing Carbon Penetration. × 100

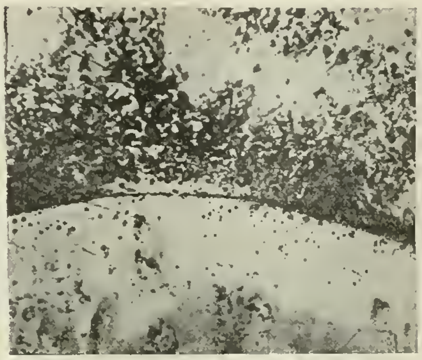

Fig. 23—Steel (P 1.06%) in Carbon Steel. Two Air Pockets Separated by Line of Good Contact. Copper Reagent. × 50

of ordinary steel. Figs. 17 and 18, at 100 and 12 diameters, respectively, illustrate this very marked effect. A wide ferrite ring, uniform in width, is shown in both figures. Fig. 18 was made without using the ocular of the microscope and the definition is not good, but the etching effect is easily seen.

SILICON—In Fig. 19 the effect of silicon is shown. The ferrite patches about the insert are very wide in places, and very irregular. The irregularity is, no doubt, due to lack of uniformity in distribution of iron silicide in the special steel.

OXIDATION

Throughout this discussion it has been assumed that diffusion of the special element or compound from the insert into the adjacent steel has been the cause of ferrite segregation near the contact surface. It is worth while to inquire whether oxidation may have had some influence, through leakage of air into minute cavities caused by badly fitting inserts, with resulting oxidation of carbon. Five lines of evidence lie against this possibility:

1—Microscopic examination of the polished section easily discloses points of poor contact, and ferrite segregation is almost invariably most marked where contact is closest.

2—Oxidation should act upon steel insert and body alike. If the inner lining of the hole in the body is to be decarburized by oxidation, the outer layers of the insert also should be decarburized, where the insert is of steel. Figs. 5, 6, 8, 9, 16, 17, and 18 very strikingly dispose of this question. Fig. 14 gives no evidence on this point, because the etching that is appropriate for the plain carbon steel does not bring out the grain structure of the phosphorus steel.

3—It would require a continuous inflow of air to the entire lining of the cavity to produce such a regular and continuous ferrite band as was produced in many of the experiments, notably with inserts of aluminium bronze, stellite, and manganese steel, where the contact was exceptionally good.

4—The actual amount of carbon that could be oxidized by the minute amount of air enclosed in an occasional cavity, caused by using a poorly fitting insert, is necessarily small, and migration of iron carbide would quickly replace that destroyed by oxidation. Fig. 20 shows a pronounced air pocket between a plain carbon steel and a brass insert, while Fig. 21 illustrates a similar condition with the special phosphorus steel insert already discussed. In both cases any carbon that has been removed by oxidation has been replaced by carbide migration, so that pearlite grains extend to the very border of the cavity.

This ability of iron carbide to migrate readily is, of course, well known, and it is the basis for such commercial processes as case carburizing. That iron carbide can easily and continuously cross the border joining these metallic inserts with surrounding steel is, finally, illustrated by using an insert of Armco ingot iron. After giving this specimen the same treatment as was given the others, pearlite was found over the entire cross section of the insert. This is shown in Fig. 22. This is sufficient proof of perfect metallic contact.

5—Actual diffusion of iron phosphide from the special phosphorus steel is shown by use of Stead's copper reagent. Fig. 23 is from a photomicrograph taken to include two regions where there was no contact, separated by a short line of good contact. It is only into the region immediately outside the contact surface that phosphide has migrated, as is shown by the absence of a copper deposit. It may be noted also that the bright surface here shown is of approximately the same width as the ferrite ring shown for this same specimen in Fig. 14.

In addition to the experiments above described, a few metals and alloys used as inserts in heat-treated steels have failed to give any striking results. Whether this has been due to (*a*) failure to heat to the necessary temperature, (*b*) extremely low migration velocities of the special elements or compounds, or (*c*) absence of any effect of diffused material, is not now clear. These materials and others will be used for additional experiments.

SUMMARY

A considerable number of alloys and special steels have been turned into small rods and driven into holes in carbon steels, the whole assembled specimen then being heated to temperatures above the transformation range for the steel. The section of the slowly cooled piece then shows, in nearly all cases, ferrite segregation around the insert. The hypothesis that has been advanced to explain this phenomenon is to the effect that the special element, elements, or compounds have diffused into the surrounding steel, and that they have there exerted an influence toward throwing ferrite out of the austenitic solution when the latter cools into the transformation range.

These experiments are cited as possibly throwing some light upon the character of the influence of nonmetallic inclusions upon ferrite segregation. The inclusion must have a certain slight solubility in austenite, and the concentration of the dissolved matter is therefore greatest in the immediate vicinity of the inclusion. There must also be equilibrium products of reactions occurring between the material of the inclusion and the steel. These products also must have a slight solubility, and they also are localized about the inclusion. Such a condition of localized dissolved impurities might have the effect of starting ferrite crystallization first about the inclusion, thus breaking down the state of ferrite supersaturation that always occurs in hypoeutectoid steels between the temperatures A_3 and Ar_3.

If these hypotheses are correct it is easy to see the importance of uniform distribution of all elements of carbon steel, as well as of alloy steels, as otherwise it is not possible to have uniform carbon distribution, and the finished piece cannot be brought into its best condition by any ordinary heat treatment.

The effect of phosphorus upon carbon distribution is then but one illustration of the general law. Practically all of the elements that can enter steel can exert a similar influence. The importance of this fact in connection with the subject of nonmetallic inclusions comes from the fact that the inclusion furnishes a continuous supply of the dissolved impurity, and that therefore no amount of heat treatment can cure its evil effects, while the opposite is true with the dissolved element or compound that is not associated with discrete particles of inclusions.

AN ELECTROMETRIC METHOD FOR DETECTING SEGREGATION OF DISSOLVED IMPURITIES IN STEEL[1]

By E. G. Mahin and R. E. Brewer

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Received July 23, 1920

As a result of work described in two earlier papers[2] it was concluded that segregation of dissolved material derived from nonmetallic inclusions, as well as dissolved phosphides, silicides, sulfides, and elements of alloy steels, causes carbon segregation in steel, iron carbide usually leaving the region of higher concentration of impurity as the steel cools from above Ar_3.

In such a case the ferrite grains of the regions so contaminated should possess a solution tension different from that of purer grains in other parts of the steel body. An electrolytic cell in which two of such grains form the electrodes against a common electrolyte, as for example

impure ferrite–KCl–pure ferrite,

should generate an electromotive force which could be measured by use of a suitable potentiometer system.

It is manifestly impossible to isolate two ferrite grains of a given piece of steel in such a way as to make an e. m. f. measurement of such a cell practicable. On the other hand, it should be possible, at least in principle, to make successive measurements of the e. m. f. of each of two systems, in each of which a standard calomel or hydrogen electrode is connected against the grain in question, the same electrolyte being used in the two cases. In this way a comparison could be made of the electrode potentials of various grains of apparently pure ferrite and differences in degree of purity detected.

PRECAUTIONS TO BE OBSERVED

Many precautions must be observed in the attempt to apply this method in practice. Some of these may be enumerated briefly as follows:

1—Immersion of the specimen in the electrolyte is, obviously, not practicable. It then becomes necessary to pick out certain areas in the polished and etched section, making contact of the electrolyte with these alone. The microscope must be used for observation of the specimen, and an extremely fine point of some sort must be used for touching the grain under investigation, this point carrying the solution of the electrolyte and establishing the necessary connection with the remainder of the circuit.

2—In any electrode-potential measurement, contact of electrode with electrolyte must be maintained for a certain period of time, in order to establish equilibrium conditions. Using the method here discussed, it then becomes necessary to maintain a microscopic point or tube in contact with the grain under observation for some time. This presents considerable mechanical difficulties.

3—Evaporation of water from the solution at the point changes the concentration of the electrolyte at the contact surface. Using a molar solution of potassium chloride, the relative change in concentration is not serious except in case measurements of a high degree of precision are desired.

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[1] Presented at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

[2] This Journal, **11** (1919), 739; **12** (1920), 1090.

4—The positive component of the double layer over the electrode contains ferrous ions, but oxidation of these ions occurs to some extent during the time that is required for equilibrium to be established. To prevent this a current of hydrogen was directed over the specimen during the earlier experiments. It was soon found that this made little observable difference in the values obtained and its use was discontinued.

5—Polishing produces a layer of amorphous metal over the crystalline structure underneath, according to the now generally accepted theory of Beilby.[1] This amorphous (strained) material is slightly more positive than crystals of the same material.[2] This layer is removed by etching, so that it should have no effect upon experimentally determined values.

6—Etching the specimen with nitric acid in alcohol might, conceivably, produce a condition of slight passivity of the iron. This was tested by comparing the potential of such a specimen with that of the same specimen etched with alcoholic hydrochloric acid, a less satisfactory etching solution from the standpoint of clearness of the etched surface. There was no consistent difference between the two sets of values.

7—Exposure of the surface to the air before testing gradually raises the electrode potential by oxidation. This interference was avoided by polishing and etching each specimen just before making the measurements.

Greater precautions with regard to all of these points would have to be taken if a high degree of precision were required. But even in the purest steel there will be so much variation in either ferrite or pearlite grains, from point to point, that values will probably have little significance beyond the third, or possibly even the second, decimal place.

EXPERIMENTAL

APPARATUS—Fig. 1 illustrates the manner of assembling the apparatus, the illuminating system and potentiometer being omitted from the drawing. The specimen under investigation had a short copper wire soldered to its lower surface, this wire dipping into a cup of mercury placed beneath the stage of the microscope. This made a connection with the potentiometer which permitted focusing the stage of the metallographic microscope at will. The specimen was held by a Sauveur magnetic holder. This, of course, resulted in grounding the specimen through the microscope. Experiments carried out with the specimen insulated from the microscope and with a nonmagnetic holder showed that neither of these factors affected the observations of the e. m. f. in the third decimal.

The electrolyte was a molar solution of potassium chloride in boiled distilled water. A solution of ferrous sulfate is not suitable for this purpose because of the facility with which hydrolysis and oxidation take place. A clear solution cannot be kept without having an excess of acid present.

Contact with the specimen was made by means of a very fine, capillary, glass tube, G, drawn to hair-like dimensions. An attempt was first made to use a porous or tubular fiber, either animal or vegetable, cemented in the end of a fine tube. No success has as yet been attained in this direction. Further experiments along this line are in progress. Fig. 2 will indicate the appearance of the capillary point as applied to one of the ferrite rings obtained in the course of the work described in the second paper dealing with this subject.[1] It will be noticed that only the tip of the tube is in focus, so that the grain structure of the steel is visible through the upper part of the tube.

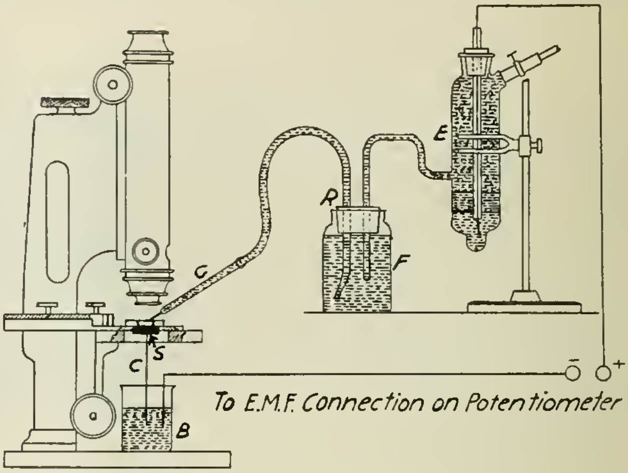

Fig. 1—Assembled Apparatus
B—mercury; C—copper wire; S—specimen of steel; G—glass tubing with capillary point; R—rubber tubing; F—molar KCl; E—normal calomel electrode

A normal calomel half-element completed the electromotive system, and a Leeds and Northrup precision potentiometer, with wall-type galvanometer having a sensitivity of 93 megohms, was used for making the measurements by the Poggendorff compensation method. The apparatus was shielded from the interference of stray fields by the method of White.[2]

For the illumination of the microscope an Ediswan "Pointolite" lamp, 100 candle power, was used, the light passing through the usual condensing system to the 45° reflector in the microscope.

RESULTS—The measurements that have been made to date would indicate that this method has possibilities for research purposes, although it is not considered likely to have any particular value as a routine testing method. Many variable and unsatisfactory results were obtained during the early part of the work and changes in the apparatus were made to meet difficulties that developed. A single set of measurements will be cited to show the nature of the results. These measurements were made on a piece of carbon steel containing an insert of aluminium bronze, the specimen having been heated to 850° C. for 7 hrs. and cooled in the furnace. The appearance of the polished and etched section is shown in Fig. 3.

In the table each group of values represents a series of readings of the e. m. f. of the system for a given microscopic spot on the steel section, the values increasing as the readings are repeated. In each group the value marked with an asterisk is the maximum value, the reading remaining constant to three decimals for 30 sec. The first column contains values, in volts, of the e. m. f. for various points on the ferrite ring X of Fig. 3. In the second and third columns are given values for various points on the body Y of the steel.

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[1] *Proc. Roy. Soc.*, **72** (1903), 227.

[2] Lord Kelvin, *Phil. Mag.*, **46** (1898), 82; Hambeuchen, University of Wisconsin, *Engineering Bulletin* **2** (1901), 235; Jackson, *Trans. Am. Soc. Mech. Eng.*, **22** (1900–1901), 816.

[1] This Journal, **12** (1920), 1090.

[2] *J. Am. Chem. Soc.*, **36** (1914), 2011.

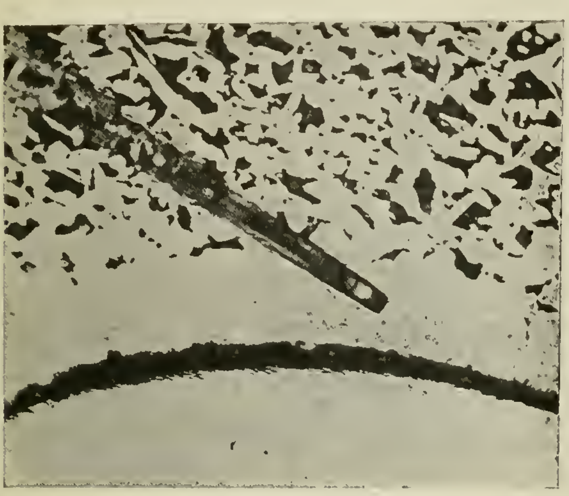

Fig. 2—Glass Capillary Point Applied to a Ferrite Ring. × 50

For the last-named points, an effort was made to restrict the contact to ferrite grains. Where the grains were small it was not always possible to do this, but the results are not appreciably affected by contact of the solution with pearlite grains, since pearlite is a conglomerate of ferrite and cementite, and since ferrite is the more positive of the two substances.

Table I—E. M. F. in Volts, for Steel with Aluminium Bronze Insert

Different Points on Ferrite Ring	Different Points on Body of Steel	Different Points on Body of Steel (*Cont.*)
0.438	0.481	0.506
0.456	0.483	0.510
0.471	0.486	0.514
*0.471	0.497	0.519
	0.560	*0.519
0.456	*0.560	
0.467		0.421
0.471	0.504	0.498
0.483	0.503	0.509
0.485	0.512	*0.509
*0.485	0.516	
	0.520	0.447
0.437	0.521	0.468
0.456	*0.521	0.475
0.457		*0.475
*0.457	0.494	
	0.510	0.510
0.379	0.537	0.512
0.435	0.541	0.514
0.459	0.543	0.518
0.464	*0.543	0.519
0.466		*0.519
*0.466	0.432	
	0.452	
0.451	0.500	
0.454	0.501	
0.478	*0.501	
*0.478		
	0.507	
	0.517	
	0.523	
Average of Maximum Values for Ferrite Ring	0.533	Average of Maximum Values for Body of Steel
	0.536	
	0.541	
	0.552	
0.471	*0.552	0.522

There is considerable variation between the maxima for the different groups in a given column. This, it would seem, might be expected, since we are dealing with a material whose composition must vary from point to point. Even upon the assumption that copper and aluminium have passed into the steel mass, thus causing the appearance of the ferrite ring, it is not to be supposed that the concentration of these metals in the ring is at all a constant quantity. The electrode potential would then be somewhat variable, and the e. m. f. of the system would vary accordingly.

Ferrite grains in the body of the piece, so far removed from the alloy insert as to preclude the possibility of contamination, are also undoubtedly impure. They probably contain most of the phosphorus and silicon of the steel, as well as traces of other impurities, and their electrode potentials also will vary.

Considering both of these probabilities it is yet significant that the starred values for the ferrite of the body of the steel are distinctly higher than those for the ferrite ring.

ELECTRODE POTENTIAL

Using 0.560 volt for the value for the calomel half-element, it will be seen that the electrode potentials for the metal, as calculated from these results, have negative values. The average for the ferrite ring is 0.471 — 0.560 = — 0.089 volt, and for the body of the piece, 0.522 — 0.560 = — 0.038 volt, a difference of about 0.05 volt. This is not in agreement with most of the values that have been found by others for iron. Walker and Dill[1] found the value 0.156 volt for unstrained Swedish iron in a ferrous sulfate solution, whose concentration was not stated. This value indicates that the solution was positive to the metal, the opposite of which is true in our measurements. Other recorded results vary somewhat from those obtained by Walker and Dill, but variations in purity, occluded gases, etc., are largely responsible.[2]

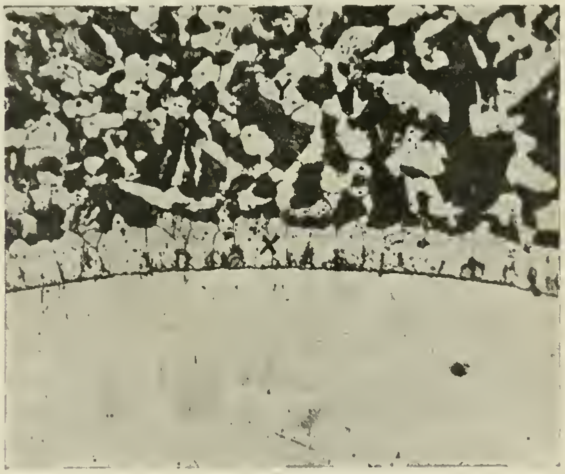

Fig. 3—Steel Adjoining an Insert of Aluminium Bronze, Heated for 7 Hrs. at 850° C. × 100

It was at first thought that this indicated an error in the method of reading, but a comparison of the electrode potential of a sample of polished and etched ingot iron made by the point-contact method above described and by immersion of the specimen in the electrolyte, shows that the immersion method gives higher readings, more nearly in accord with the results of others for practically pure iron in ferrous sulfate. It will then be concluded, either (*a*) that the point-contact method does not give true equilibrium values, contact being made for too short a time, or (*b*) that surface tension or some similar influence consistently lowers the actual potential of the grain under observation. The latter hypothesis seems not unlikely, in view of the fact that in approximately the same time period the e. m. f. values for the system containing the immersed specimen of ingot iron were considerably higher than those obtained by point contact. It is not likely that absolute equilibrium has been reached in any case, but the starred values were not changing to the extent of 0.001 volt in 30 sec. Longer contact than a few minutes is not practicable, evaporation and oxidation then serving to render the results undependable.

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[1] *Trans. Am. Electrochem. Soc.*, **11** (1907), 153.

[2] See also Richards and Behr, "The Electromotive Force of Iron, and the Effect of Occluded Hydrogen," Pub. Carnegie Inst., **1906**.

SUMMARY

A method has been developed for measuring the electrode potential of a single grain or microscopic point on a metal specimen. Results so far obtained show lower values than are given when a pure metal is immersed according to the usual scheme. No reason for this has been demonstrated, but it is shown that fairly consistent values may be obtained on a given kind of material.

When the method is applied to a piece of steel containing a segregated ring of ferrite, produced by heating in contact with aluminium bronze, it is found that average values for the ferrite ring are 0.051 volt lower than for ferrite in the unaffected body of the steel. This indicates a different degree of purity for ferrite under the two conditions, and sustains the theory already advanced to account for the ferrite ring. It is hoped that the method may be improved so that it may be applied to the exploration of the regions adjoining nonmetallic inclusions in ferrite, as well as the segregated masses of ferrite often found in steels but not associated with inclusions.

INFLAMMABILITY OF JETS OF HYDROGEN AND INERT GAS[1]

By P. G. Ledig

Bureau of Standards, Washington, D. C.

Received July 29, 1920

The purpose of the experimental work herein described was to determine the maximum amount of hydrogen which could be used with helium in balloons without losing the advantage of noninflammability. Preliminary experiments to determine the inflammability of a jet of hydrogen and inert gas under various conditions were made with hydrogen and nitrogen, in order to save helium. Later work showed that, as was supposed, there was not a great enough difference in the behavior of the gases to make it necessary to use helium throughout.

The gas mixtures were made up in a water-sealed gasometer (a meter prover) with a capacity of somewhat over 5 cu. ft. A scale on the tank was calibrated in tenths of a cubic foot. A large valve opened into a vertical cylindrical chamber about 10 cm. in diameter and 30 cm. long, with clamps at the open upper end by which steel orifice plates could be fastened in place. There were six of these orifice plates, 2 mm. in thickness, having circular orifices of 5, 10, 15, 20, 25, and 30 mm. diameter, respectively.

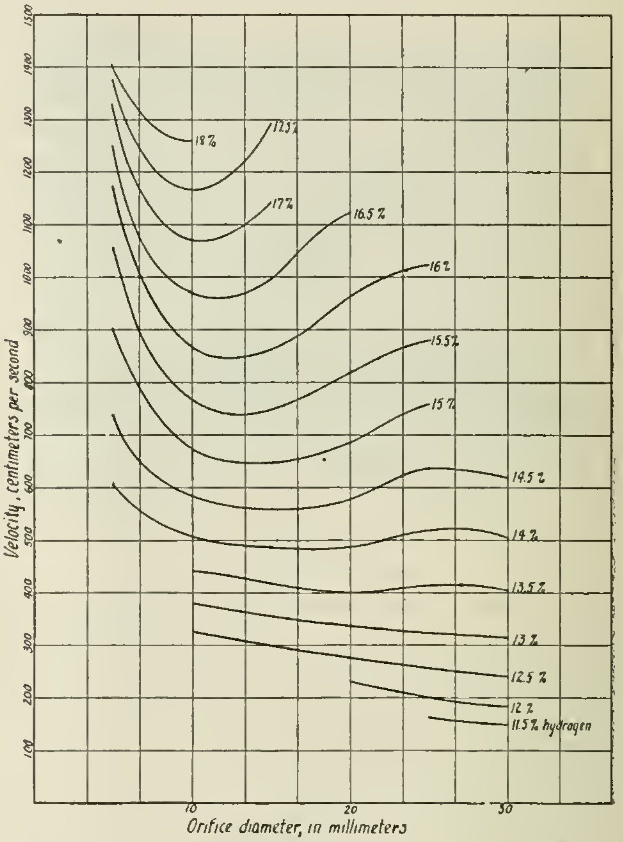

FIG. 1—RELATION OF BLOW-OFF VELOCITY TO ORIFICE DIAMETER AND HYDROGEN CONTENT

A gas mixture of approximately the composition desired was allowed to stand in the gasometer for a period of half an hour or more to permit diffusion of the hydrogen and nitrogen. The gas was then analyzed for hydrogen content, with an accuracy of 0.1 per cent. The orifice chamber was now swept out with this gas and the gas stream was then slowed down sufficiently to permit ignition or proof that the gas mixture would not burn in air. A small jet of burning coal-gas was used to ignite the gas stream. If the mixture burned, the valve was slowly opened until the velocity of the gas stream extinguished the flame by blowing it from the orifice. Since the hydrogen flame was practically invisible, it was usually found most convenient to judge this blowing-off point by sound. The flame fluttered more and more loudly as it approached the blowing-off velocity. After the flame had blown off, the valve was left open at the same position, and the gas velocity measured immediately by timing with a stopwatch the fall in the gas holder during the discharge of a definite quantity of gas. In practically all cases there was sufficient gas in the tank to make from three to five determinations with a single orifice.

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[1] Published with permission of the Director of the Bureau of Standards.

By repeating the procedure with all the orifices and over ranges of composition from the lower limit of combustibility up to varying upper percentages of hydrogen (depending upon the orifice diameter), the curves of Fig. 1 were obtained. This shows the effect of changes of composition and orifice diameter upon the blow-off velocity of hydrogen-nitrogen mixtures.

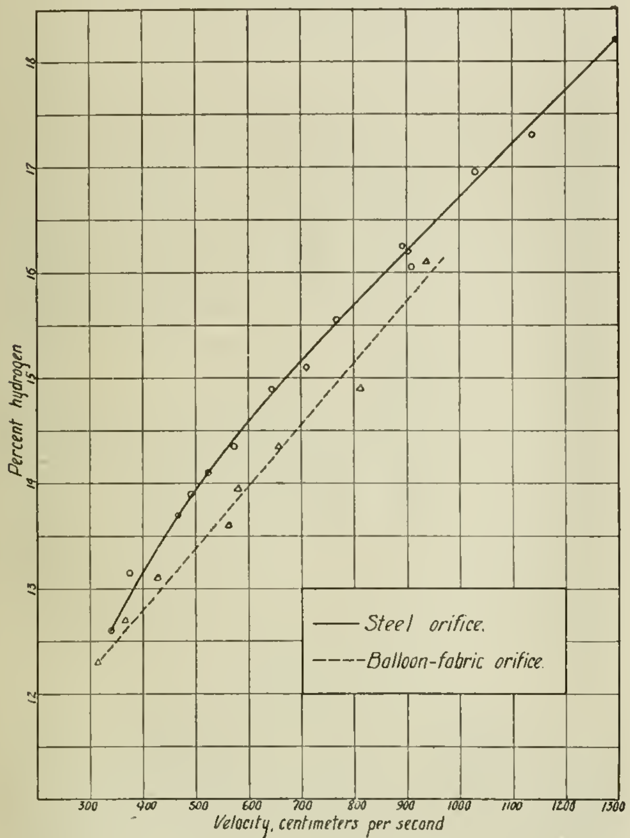

Fig. 2—Effect of Using a Balloon Fabric Orifice, 10 Mm. in Diameter

It will be seen that, for gas mixtures near the inflammable limit, the velocity at which the flame is extinguished is practically the same for orifices from 10 to 30 mm. in diameter. It is certain that the velocity at which the flame is extinguished will be less and less affected by the size of the orifice the larger the size becomes. This is true because the only conceivable effect of the size of the orifice upon inflammability is due to the influence of one portion of the flame cap upon neighboring portions, and such mutual influence is rapidly eliminated as the size of the flame is increased.

In order to determine whether any great difference is produced by using balloon fabric instead of metal for orifice material, a series of tests was run with an orifice 10 mm. in diameter cut in standard dirigible fabric. Fig. 2 shows the results of these tests. The hole in the balloon fabric enlarged scarcely at all under the influence of the slight heat from these flames, even after a considerable number of determinations were made with it. A mica orifice gave results identical with those obtained with the steel orifice, which indicates that conduction of heat by the orifice plate has little or no effect upon the blowing-off velocity for orifices as large as those used.

In the final experiments, nitrogen was replaced by helium containing about 5.5 per cent of nitrogen. The 15-mm. steel orifice was used in this series of determinations. The curve for blow-off velocity follows quite closely that of the hydrogen-nitrogen mixtures (Fig. 3). There is a difference of about 2 per cent of hydrogen in the lower limit of inflammability, however, 12.5 per cent being the lower limit in the hydrogen-nitrogen mixtures, and 14.5 per cent being the lower limit in hydrogen-helium mixtures.

In order to obtain an idea of the pressures in a balloon which would produce the gas-stream velocities necessary to blow off a flame, a series of calculations was made upon the results shown in Fig. 3, using the following equation:

$$P_o = p \frac{1}{\left[\dfrac{-S^2}{2\,\theta\, C_p}\right]^{\frac{K}{K-1}}}$$

P_o = Pressure inside the orifice
p = Pressure outside the orifice
S = Gas-stream velocity (cm. per second)
θ = Absolute temperature of the gas
C_p = Specific heat of the gas at constant pressure (ergs per gram)
K = Ratio of the specific heats of the gas $\left(\frac{C_p}{C_v}\right)$

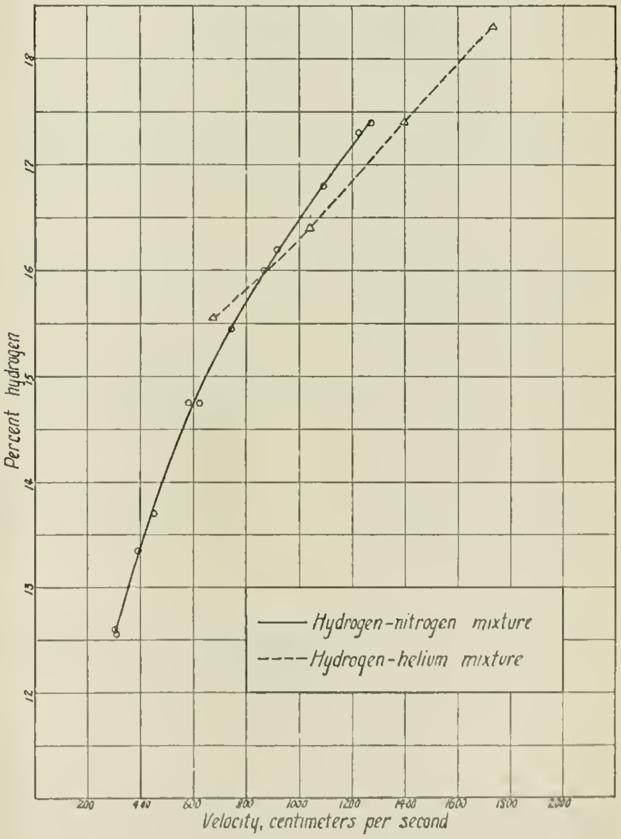

Fig. 3—Comparison of Blow-Off Velocities for Hydrogen-Nitrogen Mixtures with Those for Hydrogen-Helium Mixtures, 15 Mm. Orifice

In Fig. 4 the pressures so computed are plotted against percentage of hydrogen in the gas mixtures. Since the gas pressures in a balloon are equivalent

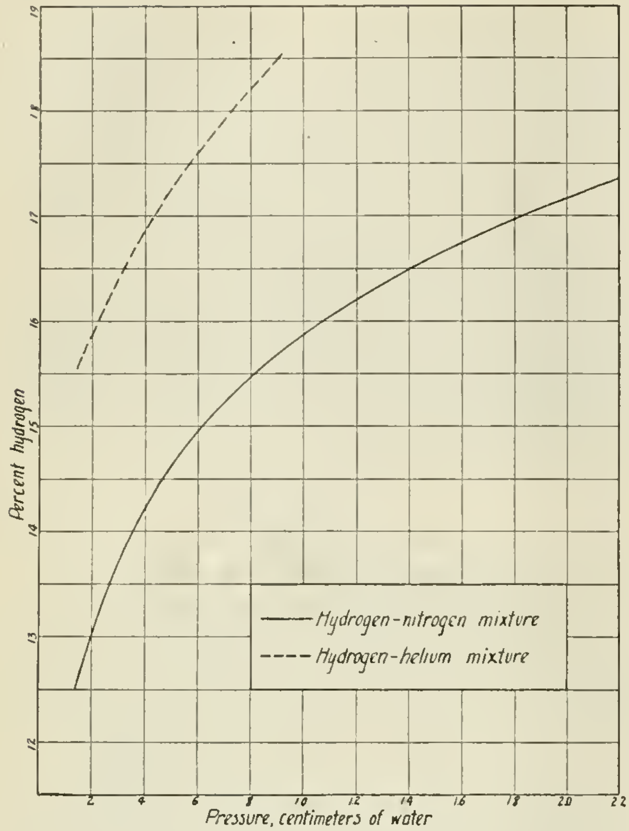

Fig. 4—Gas Pressures Required to Produce the Blow-Off Velocities Shown in Fig. 3

to several centimeters of water, the results indicate that as high as 18 per cent hydrogen can safely be used to dilute helium when it is used in balloons.

CONCLUSIONS

1—Under the most favorable conditions, a jet of helium containing more than 14 per cent of hydrogen can be ignited in the air.

2—Eighteen to twenty per cent of hydrogen may be mixed with helium, without producing a mixture which will burn with a persistent flame when issuing from an orifice under the conditions prevailing in balloon practice.

3—More than 20 per cent of hydrogen in a hydrogen-helium mixture cannot be used in a balloon without sacrificing safety from fire.

THE REACTION BETWEEN SELENIUM MONOCHLORIDE AND ETHYLENE

By F. H. Heath and Waldo L. Semon
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Received July 17, 1920

In the attempt to prepare the selenium analog of β,β'-dichloroethyl sulfide (mustard gas), it was necessary to prepare selenium monochloride and to attempt the preparation of selenium dichloride.

PREPARATION OF SELENIUM MONOCHLORIDE

The method of direct union of chlorine and selenium suggested by Beckmann[1] was found to give a product too impure for use, since it contained much free selenium and considerable selenium tetrachloride. The reaction of selenium in sulfuric acid and hydrogen chloride as reported by Divers and Shimose[1] yielded a very good product, but was much too slow for the preparation of large quantities of selenium monochloride.

The method, as finally worked out, consisted in dissolving 100 g. of selenium in 300 g. of 30 per cent oleum. This solution was placed in a distilling flask connected to a condenser, and a stream of dry hydrogen chloride, prepared by dropping concentrated hydrochloric acid into concentrated sulfuric acid, was led in. The flask was now gently heated, at a temperature low enough so that little of the selenium volatilized, and the current of hydrogen chloride was made rapid enough so that a steady stream of selenium monochloride distilled over. In this way, one run (130 g. of Se_2Cl_2) could be made in about 2 hrs. time. The sulfuric acid for making the hydrogen chloride was reconcentrated and used over and over again.

The crude product was purified by shaking with successive small portions of fuming sulfuric acid until the acid layer did not show the characteristic green color of $SeSO_3$. The selenium monochloride was allowed to stand over dry sodium chloride for a week and then decanted into tubes which were sealed and kept until needed.

The reaction according to Divers and Shimose is as follows:

$$Se + SO_3 = SeSO_3$$
$$2SeSO_3 + 2HCl = SeSO_3SeCl_2 + H_2SO_3$$
$$SeSO_3SeCl_2 + HCl = Se_2Cl_2 + SO_2HOCl$$

An attempt was made to prepare selenium dichloride by passing chlorine into the monochloride until the theoretical gain in weight was obtained. The product consisted of a mixture of selenium monochloride and selenium tetrachloride and was found to react with ethylene the same way as the monochloride, but with smaller yields.

REACTION BETWEEN ETHYLENE AND SELENIUM MONOCHLORIDE

On leading a slow stream of ethylene into selenium monochloride, the liquid became warm, selenium was precipitated, and hydrogen chloride was evolved. When the reaction was complete, hot chloroform was added, and the selenium was filtered off. On cooling, long, white, needle-like crystals were precipitated. Upon recrystallization from chloroform they had the characteristic selenium odor, and were found to melt with decomposition at 118° (uncorr.). On analysis the following results were obtained:

	No. of Analyses	Found Per cent	Theory for $C_4H_6Cl_4Se$ Per cent
Carbon	1	18.1	17.5
Hydrogen	1	2.9	2.2
Chlorine	4	51.7	51.6
Selenium	2	28.56	28.8
Total		101.26	100.1

This shows the compound to be $C_4H_6Cl_4Se$.

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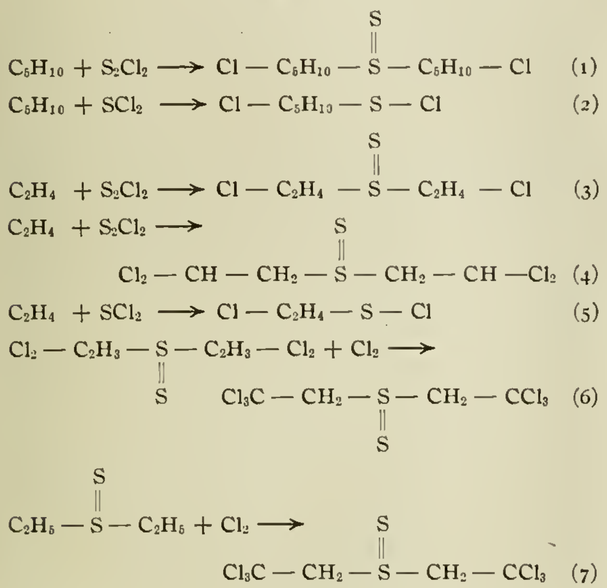
[1] *Z. physik. Chem.*, **70**, 1.

[1] *Chem. News*, **49** (1894), 212.

When ethylene was led into a carbon tetrachloride solution of selenium monochloride or into the attempted selenium dichloride, the same product was obtained, but in smaller yields.

To establish the structural formula of $C_4H_6Cl_4Se$, we may reason by analogy from the sulfur compounds. In the following equations may be found a brief resumé of the work done by Guthrie,[1] as interpreted in the light of our modern knowledge of chemistry.



$$C_5H_{10} + S_2Cl_2 \longrightarrow Cl-C_5H_{10}-\overset{\overset{S}{\|}}{S}-C_5H_{10}-Cl \qquad (1)$$

$$C_5H_{10} + SCl_2 \longrightarrow Cl-C_5H_{10}-S-Cl \qquad (2)$$

$$C_2H_4 + S_2Cl_2 \longrightarrow Cl-C_2H_4-\overset{\overset{S}{\|}}{S}-C_2H_4-Cl \qquad (3)$$

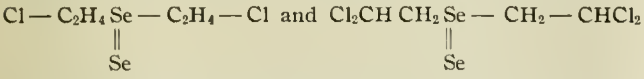
$$C_2H_4 + S_2Cl_2 \longrightarrow Cl_2-CH-CH_2-\overset{\overset{S}{\|}}{S}-CH_2-CH-Cl_2 \qquad (4)$$

$$C_2H_4 + SCl_2 \longrightarrow Cl-C_2H_4-S-Cl \qquad (5)$$

$$Cl_2-C_2H_3-\underset{\underset{S}{\|}}{S}-C_2H_3-Cl_2 + Cl_2 \longrightarrow Cl_3C-CH_2-\underset{\underset{S}{\|}}{S}-CH_2-CCl_3 \qquad (6)$$

$$C_2H_5-\overset{\overset{S}{\|}}{S}-C_2H_5 + Cl_2 \longrightarrow Cl_3C-CH_2-\overset{\overset{S}{\|}}{S}-CH_2-CCl_3 \qquad (7)$$

Further work by Frederick Kont-Norwall[2] shows that one selenium from selenium monochloride may readily be split off from its compounds, as is sulfur in the manufacture of mustard gas. Equations 3 and 4 show how the reaction between ethylene and selenium monochloride may quite probably run. Although we have no evidence of the existence of the compounds



$$Cl-C_2H_4\underset{\underset{Se}{\|}}{Se}-C_2H_4-Cl \text{ and } Cl_2CH\,CH_2\underset{\underset{Se}{\|}}{Se}-CH_2-CHCl_2$$

it is quite probable that they may be formed and the final product be $Cl_2CH.CH_2.Se.CH_2.CHCl_2$. Equations 6 and 7 show the symmetry of the atom, and by analogy the selenium compound is assumed to be likewise symmetrical.

PHYSIOLOGICAL EFFECTS

Although the physiological effects of this compound have not been studied, the experimenter has been continually troubled with water blisters on his hands while doing this work. A person working with this compound is also liable to be overcome with a sense of drowsiness. Whether this be due to the compound or to some by-product is not known.

CONCLUSIONS

1—A simple method for the preparation of selenium monochloride has been described.

2—$C_4H_6Cl_4Se$ has been prepared and it has been shown to be symmetrical tetrachlorodiethyl selenide.

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[1] *J. Chem. Soc.*, **12**, 109; **13**, 35, 135.

[2] *Oesterr. Chem.-Ztg.*, **16**, 288.

NOTE ON CATALYSIS IN THE MANUFACTURE OF ETHER[1]

By Hugo Schlatter

Hercules Powder Co., Wilmington, Delaware

Received August 18, 1920

Senderens,[2] discussing the action of aluminium sulfate as a catalyst in the manufacture of ether, states that the addition of about 5 per cent of the anhydrous sulfate to the usual mixture of sulfuric acid and alcohol lowers the temperature at which regular and rapid evolution of ether takes place from 140° C. to 130° C. He explains this action by assuming the formation of a double aluminium ethyl hydrogen sulfate ($Al_2(SO_4)_3.SO_4HC_2H_5$), which breaks up at a lower temperature than ethyl sulfuric acid.

Although in plant operation the temperature of the still at which regular and rapid evolution of ether takes place is about 125°, it was thought of interest to determine whether the addition of aluminium sulfate would result in lowering this temperature still further, or in increasing the capacity of the still. During the war any increase in the capacity of existing apparatus was of supreme importance.

A small, glass, ether still with the necessary column and condensers was charged with a mixture of sulfuric acid and alcohol. After the evolution of ether had started, alcohol was fed into the still below the surface of the liquid at a rate corresponding to the ether produced. Senderens' statement, that evolution does not become regular until a temperature of 140° is reached, was confirmed. Amounts of aluminium sulfate varying from 3 to 10 per cent by weight were introduced into the still in subsequent runs, and it was found that with 5 or 10 per cent of aluminium sulfate the temperature was lowered to 130°.

A somewhat larger still of 1.5-gal. capacity was then constructed of lead and equipped with a steam heating coil, so as to approach factory conditions as closely as possible. Two runs of about 50 hrs. duration were made, one with and one without the addition of 5 per cent by weight of aluminium sulfate. The temperatures throughout the two runs were the same as in factory operation, *i. e.*, from 120° to 125°, and there was no difference in the net yield of the two runs.

When the still was opened after the completion of the run, it was found that severe pitting of the coils had occurred when aluminium sulfate was present, possibly owing to electrolytic action between the lead of the coils and the aluminium sulfate. In both cases there was a sludge of sulfates.

A short test was also made in the original glass still with broken porcelain. In this case the temperature at which regular evolution occurred was lowered to the same temperature (130°) as with aluminium sulfate in the glass still.

It is apparent, therefore, that aluminium sulfate offers no advantages over the lead sulfate which is normally present in lead ether stills, but is actually harmful, since it causes pitting and rapid failure of the coils. The action of lead sulfate could be explained by the formation of a double salt ($PbSO_4.SO_4HC_2H_5$), but the action of broken porcelain rather seems to disprove this theory and inclines us to the view that the rapid and regular evolution is due to physical or surface action. This view is strengthened by the fact that irregular evolution of ether actually commences at the lower temperature, even if no lead sulfate is present.

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[1] Presented at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

[2] *Compt. rend.*, **151** (1910), 392.

The observations recorded are interesting, also, because the choice of lead for the construction of a manufacturing still, which was made necessary by the character of the reagents, resulted in an improvement in the process that could not have been foreseen from laboratory experiments in glassware, and in fact had heretofore been largely overlooked.

Credit is due to Mr. W. M. Billing for carrying out the laboratory work.

THE HYGROSCOPIC MOISTURE OF FLOUR EXPOSED TO ATMOSPHERES OF DIFFERENT RELATIVE HUMIDITY[1,2]

By C. H. Bailey[3]

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Received July 30, 1920

It has long been known that cereals and cereal products are hygroscopic, and that their moisture content may be altered by varying the conditions of exposure. Brewer (1883) details certain experiments which establish this property. Other investigators, including Willard (1911), Neumann (1911), Guthrie and Norris (1912), Sanderson (1914), Swanson, Willard and Fitz (1915), and Stockham (1917), have studied the changes in weight and moisture content of stored flour. In none of these experiments, save those of Stockham, have the atmospheric conditions apparently been controlled throughout the period of exposure. Guthrie and Norris (1912) recorded the atmospheric humidity each day during the period that the flour was under observation, but their readings were apparently taken at one particular time each day, and hence do not represent the mean humidity for the several 24-hr. periods. Even had the latter been determined, it is doubtful if the hygroscopic moisture of the flour could be regarded as in equilibrium with the mean humidity of the atmosphere, when the humidity fluctuated as suddenly and violently as appears to have been the case.

Stockham (1917) reports the moisture content of wheat, bran, shorts, and flour exposed in a "saturated" and "dry" atmosphere, but did not employ any degrees of atmospheric humidity between these extremes. He found that a composite sample of flour exposed in a "still, saturated" atmosphere at a temperature of 23° C. (see p. 109) reached a maximum moisture content of 28.74 per cent in 9.12 days, at which time it was moldy. In a saturated atmosphere at 0° a moisture content of 34.78 per cent was reached in 17 days, which he states was not the maximum.

SIGNIFICANCE OF MOISTURE CONTENT OF FLOUR

It seemed desirable to ascertain the moisture content of flour in atmospheres of differing but constant humidity, after a period of exposure sufficiently long to permit the hygroscopic moisture of the flour to reach equilibrium with the atmosphere. Such data would be of service in a number of ways. Shippers, purchasers, and food control officials dealing with flour need more precise information concerning changes in moisture content, and consequently in the net weight of flour packages. The baker and storekeeper need such data for the same reason, and, in addition, are concerned with the indirect effect of changing moisture content upon the keeping qualities of flour on prolonged storage. Flour which reaches a high moisture content is quite likely, if kept moderately warm, to become unsound through the activity either of its own enzymes, or those of fungi, and especially molds and related forms, which develop on the moist flour. Millers may find such data of service in developing methods of controlling the atmospheric humidity in mills and certain milling machines. Milling operations of the future will doubtless include more attention to the moisture content of the streams at each stage of the process, and such control will be established in large part by maintaining the proper humidity in the air in the various machines.

METHOD OF PROCEDURE

The humidity of the atmosphere to which flour was exposed was controlled by contact with the surface of sulfuric acid solutions. These solutions were prepared after the Reynault tables in Landolt, Börnstein and Roth's "Tabellen."[1] Four solutions were prepared, which were intended to afford humidities of 30, 50, 70, and 80 per cent, respectively. It was not deemed advisable to attempt to maintain the humidity above 80 per cent because:

(*a*) The flour is apt to mold in very damp atmospheres.

(*b*) In most parts of the United States an atmospheric humidity in excess of 80 per cent is not likely to be maintained for a prolonged period.

(*c*) It becomes more difficult to maintain the humidity at a constant level when in excess of 80 per cent.

Two samples of flour were used in these studies—a patent and a second clear flour. Their chemical composition is shown in Table I.

TABLE I—COMPOSITION OF FLOURS USED IN HYGROSCOPIC MOISTURE STUDIES

SAMPLE	MOISTURE Per cent	CALCULATED TO DRY BASIS: Crude Protein (N × 5.7) Per cent	Ash Per cent	Acidity (as Lactic) Per cent
Patent........	8.71	12.44	0.47	0.159
Second clear...	9.92	16.46	2.38	0.781

Five grams of each of these flours were placed in tared, flat-bottomed, aluminium drying dishes, having a diameter of 50 mm. This quantity of flour filled the dishes to a depth of 5 to 6 mm. The dishes were placed in desiccators, the lower part of which was filled with the appropriate sulfuric acid solution. The several desiccators were set in a thermostat having a a temperature of 25°. This was the lowest temperature which could be constantly maintained in the basement rooms of the laboratory building during the spring and early summer months.

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[1] Published with the approval of the Director as Paper No. 214, Journal Series, Minnesota Agricultural Experiment Station.

[2] Presented at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

[3] With the coöperation of Miss Isabel Everts.

[1] 4th Edition, 1912, p 426.

Preliminary studies indicated that it required 6 to 8 days for the flour to reach equilibrium in moisture content. The time doubtless hinges in part on the difference between the initial moisture of the flour and that which it will ultimately attain. To insure that ample time was afforded, the dishes (all tests being carried out in duplicate) were left undisturbed for 8 days, weighed, returned to the chambers for 2 days more, and again weighed. The difference between the first and second weighings was usually small. The dishes with their contents were dried to constant weight at 100°C. *in vacuo,* and the weight of the empty dish being known, the calculation of the initial and final moisture content of the flour was then possible.

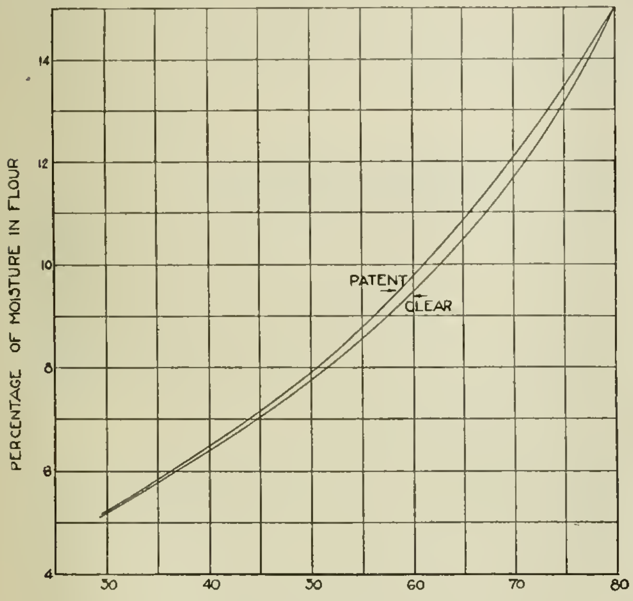

Fig. 1

At the time the dishes were finally removed from the desiccators, a portion of the sulfuric acid was drawn off and its specific gravity at once determined. From this, the percentage of H_2SO_4 could be ascertained, and the vapor pressure and relative humidity computed through the use of the tables mentioned herewith. Since it was not convenient to prepare sulfuric acid solutions of concentrations which would give exactly the humidity desired at the close of the experiments, small variations from the desired humidity were found in most cases. These deviations were always less than one per cent, in terms of relative humidity.

In Table II and Fig. 1 are shown the percentages of moisture in the patent and clear flours exposed to atmospheres of approximately 30, 50, 70, and 80 per cent relative humidity. While the differences between the two grades of flour are small, they are in the direction of a slightly higher hygroscopicity on the part of the patent grade. Stockham (1917) had previously shown (page 105) a difference in the hygroscopic moisture of starches prepared from patent and clear flours, those from the patent containing more moisture when they were exposed under identical conditions. The curves are of the shape of a simple parabola, which, if extrapolated to 100 percent humidity, would give values in terms of hygroscopic moisture not far different from those reported by Stockham for the flours exposed in a "saturated" atmosphere.

Table II—Hygroscopic Moisture of Patent and Second Clear Flours in Contact with Atmospheres of Various Humidities at 25° C. (78° F.)

Relative Humidity of Atmosphere at 25° C. Per cent	Moisture of Flour	
	Patent Per cent	Second Clear Per cent
80.0	15.00	15.00
69.8	12.05	11.65
50.3	7.93	7.81
29.4	5.18	5.11

The question at once arises as to how rapidly these flours change in moisture content with variations in the humidity of air to which they are exposed. That the response is rapid may be deduced from the experiments of Guthrie and Norris (1912). The exact rate must depend upon a number of variables, however, including the size and shape of the package in which flour is contained, the material from which it is manufactured, the extent of circulation of air about the package, and possibly other factors of minor importance. It appeared impossible to develop this phase of the investigation adequately at this time, and the study of rate of response must be deferred to a later date. Such data as were secured in certain of our preliminary studies indicate, as might be anticipated, that a dry flour placed in a humid atmosphere (or *vice versa*) changes rapidly the first 3 days, and much more slowly the next 3 days, after which, if exposed in thin layers, there is little further change.

CONCLUSIONS

Flour responds readily to changes in the humidity of surrounding air, the rate at which equilibrium in moisture content is approached depending apparently upon conditions of exposure.

Hygroscopic moisture in flour in equilibrium with atmospheric humidity at 25° C. ranges from a little more than 5 per cent of moisture at 30 per cent relative humidity to 15 per cent of moisture at 80 per cent relative humidity.

Curves representing the relation between hygroscopic moisture (ordinates) and relative humidity (abscissae) have the shape of a simple parabola, thus indicating that hygroscopic moisture does not increase at a uniform rate when in equilibrium with an increasing atmospheric humidity.

Flour testing laboratories engaged in analyzing fresh flour containing 12 to 13 per cent of moisture will experience no appreciable change in the moisture content of such flour if the relative humidity of the laboratory atmosphere is maintained in the neighborhood of 70 per cent.

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CHANGES IN THE POLARIZING CONSTANTS OF SUGARS DURING REFINING[1]

By A. F. Blake

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Received June 26, 1920

It is the purpose of this paper to discuss the changes taking place in the relationship between polarization, true sucrose, and invert sugar during the refining of raw sugar, to determine, if possible, the causes of these changes, and to point out their practical significance. As pointed out by Dr. Browne,[2] the percentage of true sucrose in a mixture of sucrose with pure invert sugar, consisting of equal parts of dextrose and levulose, will exceed the polarization at 20° C. by about three-tenths of the percentage of invert sugar. That is,

$$\frac{S - P}{I} = 0.30$$

where S represents the percentage of sucrose, P the polarization, and I the percentage of invert sugar. The factor will vary very slightly with the concentrations of sucrose and invert sugar, but a very small deviation from equality in the proportions of dextrose and levulose in the invert sugar will very greatly alter its value, because of the wide difference in the rotations of these two sugars. A value of $(S - P)/I$ above 0.30 indicates excess of levulose; a value less than 0.30, an excess of dextrose. Dr. Browne discusses the influence of temperature, maturity of cane, methods of manufacture, and length of storage of raw sugar upon the value of this ratio, and mentions the fact that in the process of refining its value is very materially reduced, and gives analyses of soft sugars and refiners' sirup, in support of this assertion.

EXPERIMENTAL PART

In Table I is shown an analysis of a cargo of Cuban raw centrifugal sugar of uniform quality and all one mark, together with the average analyses of soft refined sugar and refiners' barrel sirup produced from it. These particular analyses are selected for the purposes of the discussion because they are quite typical and because the refinery started melting this cargo following a shutdown from which practically no stock in process was brought forward, and melted this cargo exclusively for a considerable period, so that it is quite certain that the three analyses are interrelated. Dr. Browne's observation of the reduction of the value of $(S - P)/I$ is very strikingly affirmed.

TABLE I—ANALYSIS OF CUBAN RAW CENTRIFUGAL SUGAR AND OF SOFT REFINED SUGAR AND REFINERS' BARREL SIRUP PRODUCED THEREFROM

	RAW SUGAR	SOFT SUGAR	REFINERS' SIRUP
ANALYSES WET			
Polarization at 20° C.	95.87	88.47	38.40
Sucrose Clerget	96.42	88.74	40.60
Water by Drying	1.05	5.29	19.57
Invert	1.25	3.51	22.99
Insoluble	0.16	...	...
Soluble Ash	0.66	1.24	8.13
Soluble Organic	0.46	1.22	8.71
EX-WATER AND INSOLUBLE			
Polarization	97.04	93.41	47.74
Sucrose Clerget	97.59	93.70	50.48
Invert	1.27	3.71	28.58
Ash	0.67	1.31	10.11
Organic	0.47	1.28	10.83
IMPURITIES			
Invert	52.7	58.8	57.7
Ash	27.8	20.8	20.4
Organic	19.5	20.4	21.9
RATIOS			
Invert ÷ Sucrose × 100	1.30	3.95	56.6
Invert ÷ Ash	1.89	2.83	2.83
(S — P)/I	0.44	0.077	0.096

The value has fallen from 0.44 in the raw sugar to 0.077 in the soft sugar and 0.096 in the sirup. The value of 0.44 is a little above the average. This ratio is subject to wide variations, as shown by a summary of the results obtained on 32 cargoes from various sources.

No. Cargoes	From	Time Received	Condition	—Value of (S—P)/I— Minimum	Maximum	Av.
8	Cuba	June–Dec. 1919	Deteriorated	0.08	0.29	0.20
6	Cuba	Jan.–March 1920	New crop	0.44	0.73	0.55
10	Demerara	June 1919–Jan. 1920	Good	—0.03	0.34	0.16
2	Demerara	Dec. 1919–Jan. 1920	Deteriorated	0.48	0.55	0.51
6	San Domingo	June–Oct. 1919	Good	0.23	0.59	0.37
			TOTAL	—0.03	0.73	0.30

It seems that new crop sugars have higher values than the remnants of the old crop, which in this case were in general more or less deteriorated, although in some instances deterioration may be of such a nature as to increase the ratio.

WASHING—The first process of refining is one of affination or washing. The sugar is mixed to a magma with its own sirup washings, purged in centrifugal machines, and washed with water. The only result is a separation into a high-purity washed sugar and low-purity washings. It is hardly to be supposed that any change in the value of $(S - P)/I$ would take place here, though it is possible that it might differ somewhat in washed sugar and washings, since the impurities in the sirup are those of the molasses adhering to the grain, and those in the washed sugar those in the grain itself. In the latter the invert is lower and the organic higher. The analyses in Table II would indicate that there is no great change of the $(S - P)/I$ ratio in the process of affining. The determination of the ratio with great accuracy is impossible in very high-purity material such as washed sugar, since a trifling error in polarization or Clerget, say, 0.05 degree, makes a large error in $(S - P)/I$. The washings, too, being very highly colored, present some difficulties in a Clerget determination, but the

TABLE II—ANALYSIS OF FILTERED SOLUTIONS OF CUBAN RAW SUGAR AND OF WASHED SUGAR AND CENTRIFUGAL WASHINGS PRODUCED THEREFROM

	Raw Sugar	Washed Sugar	Centrifugal Washings
Dry Polarization	96.37	98.77	78.05
Dry Clerget	96.91	98.98	80.56
Dry Invert	1.20	0.43	8.35
Dry Ash	0.62	0.19	3.62
Dry Organic	1.27	0.40	7.47
(S — P)/I	0.45	0.49	0.30

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[1] Presented at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

[2] In a paper entitled "Influence of Conditions upon the Polarizing Constants of Sugar Cane Products," read at the 56th Meeting of the American Chemical Society, Cleveland, Ohio, September 10 to 13, 1918

most approved methods were used and usual sources of error eliminated as far as possible.

DEFECATION—After the washing process both sugar and washings are defecated with lime and phosphoric acid at a temperature of 180° F. and left slightly alkaline to litmus. The concentrated, bone-black filter sweet water, or char water, and the concentrated bag-filter flush water, or scum water, are also thus treated and then filtered through bag filters. Table III shows no change for (S — P)/I for washed sugar from the time of reaching the blow-ups until through the bag filters. Table IV, however, shows a slight reduction from the defecation for scum and char water, and a greater reduction for the centrifugal washings.

TABLE III—ANALYSIS OF CENTRIFUGALLY WASHED RAW SUGAR BEFORE DEFECATION AND AFTER DEFECATION AND BAG FILTRATION

	Before Defecation	After Filtration
Brix	61.25	60.62
Dry Polarization at 20° C.	98.67	98.74
Dry Sucrose Clerget	98.81	98.89
Dry Invert	0.43	0.46
Dry Ash	0.25	0.23
Dry Organic	0.51	0.42
(S — P)/I	0.33	0.33

TABLE IV—ANALYSIS OF LOW TEST MATERIAL BEFORE AND AFTER DEFECATION

	Mixed Scum and Char Water		Centrifugal Washings	
	Before Defecation	After Defecation	Before Defecation	After Defecation
Alkalinity at 32° Bé.	(0.001 *N* Acid)	0.009 *N*	0.006 *N*	0.023 *N*
Brix (Diluted and Filtered)	40.70	37.50	32.50	30.40
Dry Polarization	78.67	78.85	77.08	77.53
Dry Sucrose Clerget	78.87	78.99	78.83	78.39
Dry Invert	6.24	6.37	10.68	10.55
Dry Ash	4.72	4.80	3.01	3.13
Dry Organic	10.17	9.84	7.48	7.93
(S — P)/I	0.031	0.021	0.16	0.081

In the latter case, the material after defecation is rather more than slightly alkaline, and a slight loss of invert sugar is indicated. Heating with lime, of course, is known to destroy invert sugar, and doubtless the levulose is the ingredient most affected, thus reducing the value of (S — P)/I. From this and other analyses, however, it is not believed that any great portion of the decrease in (S — P)/I during refining is attributable to blow-up defecation.

After use, the bag filters are flushed, in this case with hot water only, producing a light material known as scum water. The mud removed from the bags is diluted with water, limed, and heated to a high temperature, and filter-pressed, yielding press water.

TABLE V—ANALYSIS OF CENTRIFUGAL WASHINGS BEFORE DEFECATION SCUM WATER, AND PRESS WATER

	Centrifugal Washings	Scum Water	Press Water
Brix	57.40	18.20	5.15
Alkalinity by $Ca(OH)_2$	0.014 *N*	0.004 *N*	0.010 *N*
Dry Polarization at 20° C.	78.56	79.68	67.38
Dry Sucrose Clerget	80.94	80.38	67.38
Dry Invert	7.77	5.65	0.33
Dry Ash	4.10	4.56	10.25
Dry Organic	7.19	9.41	22.04
(S — P)/I	0.31	0.12	0.00

Table V shows comparative analyses of the centrifugal washings last on the bag filters, the scum water, and the press water. A decrease in the ratio is to be noted, the decrease being again accompanied by loss of invert. In the case of the press water, the invert has been practically all destroyed by the liming and heating, and, as would be expected, the polarization equals the Clerget, and (S — P)/I is zero. As only a small portion of the melt is handled as scum water or press water, however, we have to look further for the main cause of the decrease of the ratio.

TABLE VI—ANALYSIS OF BAG-FILTERED MATERIAL BEFORE AND AFTER TREATMENT WITH FRESH BONE-BLACK

	Washed Sugar		Mostly Scum and Char Water	
	Before Treatment	After Treatment	Before Treatment	After Treatment
Brix	60.85	57.85	56.70	...
Dry Polarization	98.77	99.17	86.95	91.19
Dry Sucrose Clerget	98.87	99.15	87.11	90.80
Dry Invert	0.47	0.31	5.91	5.11
Dry Ash	0.24	0.13	2.35	1.26
Dry Organic	0.42	0.41	4.63	2.83
Invert Per cent Impurities	41.6	36.5	45.8	55.5
Ash Per cent Impurities	21.2	15.3	18.2	13.7
Organic Per cent Impurities	37.2	48.2	36.0	30.8
(S — P)/I	+0.21	—0.06	+0.027	—0.076

BONE-BLACK FILTRATION—Table VI shows a change in (S — P)/I on washed sugar filtered through bone-black, from +0.21 to —0.06, and on low-test bag-filtered material treated with fresh bone-black in a laboratory test from +0.027 to —0.076. It would seem that here is the real cause for the change in (S — P)/I during refining. In every test it has been found that in the case of the material first off the bone-black the polarization always exceeds the Clerget. Table VII gives progressive analyses of the various materials going on a bone-black filter and of roughly equivalent portions coming off. The value of (S — P)/I is greatly reduced on the first material, washed sugar, and progressively less so on the granulated sirups and char-filtered liquor following. The averages show a considerable loss for the whole operation. It is also to be noted that low material put on fresh bone-black, as in Table VI, suffers a large decrease in (S — P)/I, but when put on the end of a used filter the ratio is but little changed. Another point of interest is that invert is absorbed from first material and given up to later material, the whole operation resulting in no loss of invert. In this test there appears to be a slight loss of invert, but numerous other tests of like nature have shown a good balance, but always with the same transfer from first material to later material. The significance of this invert absorption will be treated shortly.

The same conclusions regarding the relation of char filtration to (S — P)/I are drawn from the analyses of three grades of soft sugar shown in Table VIII. The light yellows, boiled from liquor early off the char filters, show negative values for (S — P)/I, the brilliants boiled from later liquor show positive values, and the darks still higher values. The average soft sugar of Table I, mostly brilliants with small amounts of light and darks, shows a value in agreement with Table VIII. The high invert per cent of impurities on lights is not because invert has not been absorbed, but because the other impurities, ash and organic, have been absorbed to a much greater extent.

Subsequent to char filtration there appears to be no change in (S — P)/I. The average value for all the material off the filters is not greater than the average value in final soft sugars and barrel sirup. In Table I the value for sirup exceeds that for soft sugars because there is some light yellow, with its negative value of (S — P)/I, mixed into the average soft.

TABLE VII—ANALYSES OF MATERIAL GOING ON AND COMING OFF A BONE-BLACK FILTER

Going on Filter

MATERIAL	Washed Sugar		Granulated Sirup	Char-Filtered Liquor	Heavy Char Water	Weighted Average
Gallons	13,860	....	3,600	8,280	1,440	27,180
Solids Per cent of Total on	50.54	....	13.91	30.37	5.18	100.00
Brix	58.85	....	62.45	59.35	58.35	59.54
Alkalinity	0.003 *N*	....	0.002 *N*	0.003 *N*	0.006 *N*	0.003 *N*
Color	41.0	....	45.0	45.0	110.0	45.0
Dry Polarization	98.56	....	91.59	90.25	85.00	94.31
Dry Sucrose Clerget	98.59	....	91.75	90.47	85.36	94.44
Dry Invert	0.46	....	5.09	5.31	5.67	2.90
Dry Ash	0.29	....	1.38	1.73	3.57	1.05
Dry Organic	0.66	....	1.78	2.49	5.40	1.61
Invert Per cent Impurities	32.9	....	61.7	55.7	38.8	52.2
Ash Per cent Impurities	20.7	....	16.7	18.2	24.4	18.9
Organic Per cent Impurities	46.4	....	21.6	26.1	36.8	28.9
(Invert ÷ Sucrose) × 100	0.47	....	5.55	5.87	6.65	3.07
Invert ÷ Ash	1.59	....	3.70	3.06	1.59	2.76
(S — P)/I	0.07	....	0.031	0.044	0.063	0.045

Coming off Filter

MATERIAL	Washed Sugar	Mostly Washed Sugar	Granulated Sirups and Char-Filtered Liquor		Sweet Waters	Weighted Av. Up to "in Waste"
Gallons	10,660	2,660	3,550	10.240	3,260	30,370
Solids Per cent of Total off	38.83	9.93	13.14	36.30	1.80	100.00
Brix	59.55	60.90	60.50	57.90	9.05	53.81
Alkalinity	0.002 *N*	0.1002 *N*	0.002 *N*	0.002 *N*	(0.001 *N* Acid)	0.002 *N*
Color	1.0	5.0	11.0	20.0	9.0	10.0
Dry Polarization	99.45	97.78	94.88	90.33	60.77	94.68
Dry Sucrose Clerget	99.32	97.68	94.83	90.54	60.77	94.69
Dry Invert	0.28	1.50	3.42	5.46	4.85	2.77
Dry Ash	0.13	0.31	0.79	1.76	8.61	0.98
Dry Organic	0.27	0.51	0.96	2.24	25.77	1.56
Invert Per cent Impurities	41.0	64.5	66.1	57.7	12.4	52.2
Ash Per cent Impurities	18.5	13.5	15.3	18.6	21.9	18.5
Organic Per cent Impurities	40.5	22.0	18.6	23.7	65.7	29.3
(Invert ÷ Sucrose) × 100	0.28	1.53	3.61	6.03	7.98	2.93
Invert ÷ Ash	2.21	4.79	4.31	3.10	0.56	2.83
(S — P)/I	—0.48	—0.067	—0.015	+0.038	0.00	+0.004

The boiling in vacuum pans does not affect the ratio, if there is no inversion. Inversion, here or elsewhere, would presumably increase the ratio by addition of true invert sugar with its normal value of 0.30. That this is the case is shown in an exaggerated manner by the analysis in Table IX of a table sirup made by deliberate inversion of char-filtered liquor. (S — P)/I is 0.282 or, as would be expected, almost up to the theoretical value. A less exaggerated case is shown in Table X, where some char-filtered liquor was purposely submitted to slight inversion. The ratio has increased from 0.029 to 0.119. A subsequent treatment with bone-black reduced the ratio somewhat, but not to the original value. The value of this ratio is therefore a good indication of refinery performances.

TABLE VIII—ANALYSES OF LIGHT, BRILLIANT, AND DARK SOFT REFINED SUGARS

Lot No.	M 231	O 271	M 234	O 621	M 197	O 614
Grade	Light	Light	Brilliant	Brilliant	Dark	Dark
Polarization at 23° C.	92.50	90.55	87.85	90.00	85.55	85.00
Sucrose Clerget	92.48	90.50	88.06	90.19	85.96	85.47
Water	5.20	6.35	5.25	3.50	4.10	3.40
Impurities	2.32	3.15	6.69	6.31	9.94	11.13
Invert	1.32	1.96	3.23	2.99	5.02	5.52
Invert Per cent Impurities	56.9	62.2	48.3	47.4	50.5	49.6
(S — P)/I	—0.015	—0.026	+0.065	+0.063	+0.082	+0.085

TABLE IX—ANALYSIS OF A TABLE SIRUP MADE BY INVERSION OF CHAR-FILTERED LIQUOR

Brix	81.25
Polarization at 21.7° C.	7.10
Sucrose Clerget	22.86
Invert	55.87
(S — P)/I	0.282

TABLE X—ANALYSIS OF CHAR-FILTERED LIQUOR BEFORE AND AFTER ARTIFICIAL INVERSION, AND OF THE INVERTED LIQUOR AFTER BONE-BLACK TREATMENT

	Before Inversion	After Inversion	After Char Treatment
Brix	60.00	57.80	57.55
Dry Polarization at 21° C.	91.08	88.15	88.96
Dry Sucrose Clerget	91.20	88.82	89.49
Dry Invert	3.97	5.69	5.37
(Invert ÷ Sucrose) × 100	4.36	6.4	6.03
(S — P)/I	0.029	0.119	0.097

It has been shown that the action of bone-black is the chief cause of the decrease of (S — P)/I. Since bone-black absorbs invert from first material, where the decrease of (S — P)/I is most marked, it may be supposed that the reduction is due to a selective action of the char in removing more levulose than dextrose from the solution, although it must be borne in mind that this cannot be the only cause, since the last material, where increases of invert are shown, should also show increases of (S — P)/I, and the operation as a whole should show no change. To test this point, an artificial invert sugar solution at 60° Brix was treated with bone-black, and the proportions of dextrose and levulose before and after treatment were determined as well as might be by polarization at widely different temperatures. The results are shown in Table XI. The method of determining levulose by high-temperature polarization may not be accurate, but as both solutions were tested in exactly the same way, the results are at least comparable. The

TABLE XI—ANALYSIS OF A SOLUTION OF INVERT SUGAR BEFORE AND AFTER TREATMENT WITH BONE-BLACK

Tests made on an approximately 60 per cent solution of invert sugar made by inverting granulated sugar with HCl and neutralizing with NaOH.

86.45 g. solution to 100 cc., approximately 52 g. total sugar per 100 cc., or 40 per cent, 20 per cent each dextrose and levulose.

	Before Treatment	After Treatment
Reading ° V. at 20° C.	—63.10	—58.60
Reading ° V. at 87° C.	+ 0.20	+ 3.85
Change per ° C.	0.945	0.932
Levulose	30.6	30.2
Dextrose	30.1	31.0
Total Sugars	60.7	61.2
Levulose, Per cent Total Sugars	50.4	49.3
Dextrose, Per cent Total Sugars	49.6	50.7

$$\text{Levulose} = \frac{\text{Change per } ^\circ\text{ C.} \times 100}{0.0357 \times 86.45}$$

$$\text{Rotation due to levulose} = \frac{\text{Per cent levulose} \times 93.30 \times 86.45}{66.5 \times 26}\ ^\circ\text{V.}$$

Rotation due to dextrose = Observed reading — Rotation due to levulose

$$\text{Per cent dextrose} = \text{Rotation due to dextrose} \times \frac{66.5 \times 26}{86.45 \times 53.08},$$

where + 66.5 = specific rotation of sucrose
+ 53.08 = specific rotation of dextrose at 20 per cent
— 93.30 = specific rotation of levulose at 20 per cent

polarizations at 87° C. and the calculated proportions of dextrose and levulose show clearly that the above assumption is correct and that char absorbs levulose from invert sugar more extensively than dextrose.

Another point which should be brought to the attention of sugar refiners is this: Since the value of (S — P)/I decreases greatly during refining, while the actual quantity of invert in products is about equal to that in the raw sugar, inversion balancing invert losses, it follows that losses of sucrose figured on Clerget tests will exceed those figured from polarizations. This fact has not been generally recognized. Although all refiners know that the polarization does not equal the true sucrose, it has been supposed that loss in polarization represents closely the loss in sucrose. Also, the final value of (S — P)/I seems to be about the same, regardless of the raw sugar used, so that statements based on polarization are particularly optimistic as regards sucrose losses when the raw sugars have high values for (S — P)/I. With regard to the removal of organic nonsugars during refining, the statements based on polarizations are also very deceptive. Since the organic is ordinarily taken as the difference between 100 and the sum of the percentages of the determined constituents, it is, of course, too high where polarizations are used. It is much more nearly correct, however, in the refined products than in the raw sugar. The true removal of organic, therefore, is not as great as appears when polarizations are used in the analyses.

In this paper two causes of the changes in the polarizing constants of sugar during refining have been indicated, the destruction of levulose by the action of heat and lime, and the absorption of levulose in excess of dextrose by bone-black. It has also been stated that a further explanation of the change during char filtration is required. Dr. Browne, in a letter to the writer, suggests that there are doubtless isomeric changes by which dextrose and levulose undergo molecular rearrangements into mannose and the so-called unfermentable sugars, glutose, etc. If this is the case the phenomenon should be related more specifically to the action of bone-black.

DICYANODIAMIDE: A RAPID, DIRECT METHOD FOR ITS DETERMINATION IN CYANAMID AND MIXED FERTILIZERS[1]

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In the course of an investigation upon the changes taking place in cyanamide when used in mixed fertilizers, it was found necessary to determine accurately the quantity of dicyanodiamide (cyanoguanidine) in various fertilizer mixtures and in samples of commercial calcium cyanamide (Cyanamid). The method previously used to determine dicyanodiamide is that of Caro,[2] as modified by Hager and Kern,[3] which consists in adding to the solution of dicyanodiamide a solution of silver nitrate and then an excess of sodium hydroxide, the latter throwing down a precipitate consisting of silver cyanamide (in case cyanamide is present), silver dicyanodiamide, and a large amount of silver oxide. The nitrogen in this precipitate is determined by the Kjeldahl method. A second portion of the solution is used for the determination of the cyanamide by the method of Perotti.[1] The difference in these two values represents the dicyanodiamide nitrogen. Kappen,[2] who later investigated these methods, showed that in the determination of dicyanodiamide in samples of Cyanamid containing urea, very large errors—sometimes as high as 50 per cent—occurred, due to the inclusion of urea in the precipitate. More recently, Hene and van Haaren[3] have modified the method by dissolving the precipitate first formed in nitric acid and reprecipitating with silver nitrate and sodium hydroxide. Using mixtures of pure cyanamide, dicyanodiamide, and urea, they have obtained fairly accurate results with the modified method. At best, however, the method is tedious, involving several precipitations and washings, and a final Kjeldahl determination on the product. It is moreover open to the objection that it is an indirect method, the dicyanodiamide being determined by difference, since all the nitrogen in the precipitate not deducted as cyanamide is considered to come from dicyanodiamide. Further modifications of this method were not attempted, as it was at once apparent that the method was fundamentally unsuited to the analysis of mixed fertilizers, since the presence of ammonium salts, which these fertilizers usually contain, would prevent the complete precipitation of the dicyanodiamide upon the addition of the sodium hydroxide.

It was desirable, therefore, to devise a direct and accurate means of determining dicyanodiamide, applicable to mixed fertilizers. A large number of compounds have been tried which it was hoped would give insoluble precipitates or colored solutions when added to dicyanodiamide solutions, and a method has been evolved which seems to be admirably suited to the purpose. The method depends upon the fact, observed by the author, that when a solution of silver picrate is added to a solution of dicyanodiamide, the latter is quantitatively precipitated as a double compound of silver picrate and dicyanodiamide, $C_6H_2(NO_2)_3OAg.C_2H_4N_4$. This new double compound we have named *silver picrate-mono-cyanoguanidine.* It forms in small crystals which quickly settle out of the solution and can be separated upon a Gooch crucible very rapidly, so that the analysis can be carried out in a very short time. Neither cyanamide nor urea give any precipitate when their solutions are treated with silver picrate, and have no effect upon the analysis for dicyanodiamide. The molecular weight of the compound is 420.22, five (4.991) times that of dicyanodiamide, a fact which greatly enhances the accuracy of the method, since an error of 1 mg. in the precipitate will mean an error of only 0.2 mg. of dicyanodiamide or 0.13+ mg. of nitrogen. While silver picrate-mono-cyanoguanidine is not insoluble in water, 100 cc. dissolving 0.12 g. of the compound at 25°, the presence of an excess of silver picrate, as used in the method, renders it practically insoluble. As shown below, this procedure reduces the solubility to 0.0044 g. in 100 cc. of the resulting solution, which corresponds to 0.0009 g. of dicyanodiamide. While for ordinary work this constant error is practically negligible, if greater accuracy is desired it is best to add to the weight of the precipitate 0.0044 g. for each 100 cc. of the solution from which it was filtered.

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[1] Presented at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

[2] *Z. angew. Chem.*, **23** (1910), 2405.

[3] *Ibid.*, **29** (1916), 309.

[1] *Rend. soc. chim. ital.*, **1904**, 192.

[2] *Z. angew. Chem*, **31** (1918), 29.

[3] *Ibid.*, **31** (1918), 129.

While it was shown that silver picrate is the causative agent in producing the double compound, the use of prepared silver picrate is not at all necessary, since the mixture of silver nitrate and picric acid gives the same reaction. In fact, the latter mixture serves even better, because the resulting solution is very slightly supersaturated in respect to silver picrate, a condition which could not be secured by adding to the dicyanodiamide solution a saturated solution of silver picrate. This supersaturation is not at all objectionable, since it was found that several days elapsed before any crystals of silver picrate appeared. Solid silver picrate, moreover, is probably explosive under certain conditions.

Two curious properties of silver picrate-mono-cyanoguanidine should prove useful in the qualitative test for dicyanodiamide. We refer to the formation of a gel, which quickly changes to crystals, when silver picrate is added to solutions of dicyanodiamide containing 0.5–4.0 mg. per cc., and, second, to the unusual form of the crystals of the compound when viewed under the microscope. Since the author was unable, either by searching through the literature or by experiments upon substances which might be present in the materials investigated, to find any compounds which possess anything like these two characteristics, it appears that positive results with these two tests would serve absolutely to confirm the presence of dicyanodiamide.

A second double compound of silver picrate and dicyanodiamide, *silver picrate-di-cyanoguanidine*, $C_6H_2(NO_2)_3OAg.2C_2H_4N_4$, was obtained by using dicyanodiamide in excess and recrystallizing the product from water. The existence of this compound is of interest in the method of analysis outlined, since solutions of dicyanodiamide more concentrated than 2 mg. per cc. give results which are too low, due no doubt to the formation of some silver picrate-di-cyanoguanidine. That the correct formulas have been assigned to these compounds is shown by the analyses, and also by the fact that the weight of yellow compound precipitated in the quantitative determination of dicyanodiamide always corresponds to the formula for silver picrate-mono-cyanoguanidine. Moreover, analogous addition compounds of dicyanodiamide have been prepared. Caro,[1] working with fairly strong solutions of dicyanodiamide synthesized three double salts with silver nitrate: $AgNO_3.C_2H_4N_4$, $AgNO_3.2C_2H_4N_4$, and $AgNO_3.3C_2H_4N_4$. Subsequently, Grossman and Schück[1] prepared $CuSO_4.2C_2H_4N_4.4H_2O$, $CdSO_4.C_2H_4N_4.2H_2O$, and $HgCl_2.C_2H_4N_4$.

EXPERIMENTAL PART

PURE DICYANODIAMIDE—Dicyanodiamide was prepared by the method of Hale and Vibrans,[2] which gave a good yield of large, transparent needles which melted exactly at 205° C.

SILVER PICRATE-MONO-CYANOGUANIDINE—To a solution of dicyanodiamide, containing 0.3 g. of the compound in 500 cc. of water, were added 75 cc. of a 5 per cent solution of silver nitrate and then 500 cc. of a saturated solution of picric acid. After about a minute the solution was vigorously stirred, which caused the appearance of a yellow crystalline precipitate. The mixture was allowed to stand for about 10 min., at the end of which time the precipitation was complete and the crystals had formed a layer on the bottom of the beaker. The precipitate was collected upon a filter, washed with a little water and then with a small amount of ether, and dried at 100° for 30 min. The crystals were of a bright yellow color, very slightly soluble in cold water but much more so in hot water, slightly soluble in alcohol and acetone, and practically insoluble in ether. When heated to 235°, they softened and turned brown, and a yellow solid collected on the cooler parts of the melting-point tube.

	N	Ag
Found	23.18 23.10	26.01
Calculated for $C_6H_2(NO_2)_3OAg.C_2H_4N_4$	23.34	25.67

A second experiment using a saturated solution of silver picrate instead of the mixture of silver nitrate and picric acid yielded a precipitate which was identical with the crystals described above.

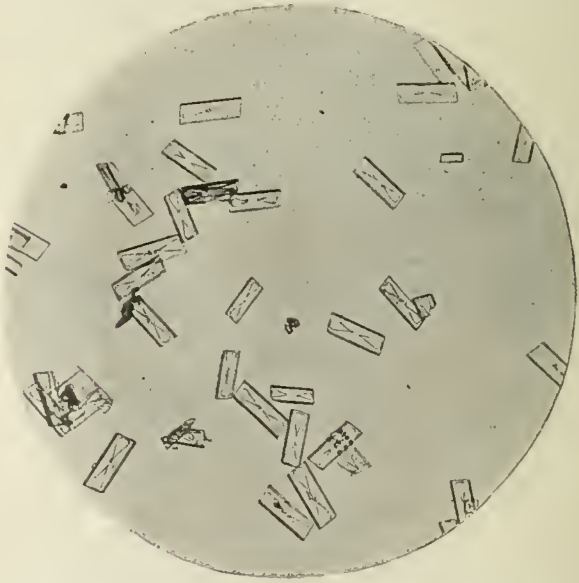

FIG. 1—CRYSTALS OF SILVER PICRATE-MONO-CYANOGUANIDINE PRECIPITATED BY ADDING SILVER PICRATE TO A SOLUTION CONTAINING PURE DICYANODIAMIDE. MAGNIFIED 120 DIAMETERS

GEL FORMATION—A solution of dicyanodiamide was prepared containing 0.1 g. of the compound in 100 cc.

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[1] *Loc. cit.*

[1] *Ber.*, **39** (1900), 3591.

[2] *J. Am. Chem. Soc.*, **40** (1918), 1057.

of water. The temperature of the solution was 20°. Fifteen cc. of 5 per cent silver nitrate were added and then 100 cc. of a saturated solution of picric acid, the latter solution also being at 20°. Almost at once the resulting solution set to a stiff jelly whose rigidity was so great that the beaker could be practically inverted without disturbing the gel. In about a minute, however, the gel began to liquefy at its edges, its mass contracting and leaving a layer of solvent between itself and the walls of the beaker. This contraction rapidly continued, and within 5 min. the gel had been entirely transformed to a crystalline precipitate which collected in a layer at the bottom of the beaker. When viewed under the microscope these crystals had the appearance shown in Fig. 1. It was found that the limits of concentration producing a good gel were from 0.6 to 4.0 mg. per cc.; solutions containing more than 4 mg. of dicyanodiamide per cc. giving a curdy precipitate. The disintegration of the gel was much retarded by employing a lower temperature, or by the presence of certain impurities found in some fertilizer mixtures, and for this reason it is advisable when analyzing mixed fertilizers to stir the solution two or three times during the first few minutes, thus avoiding the gel stage.

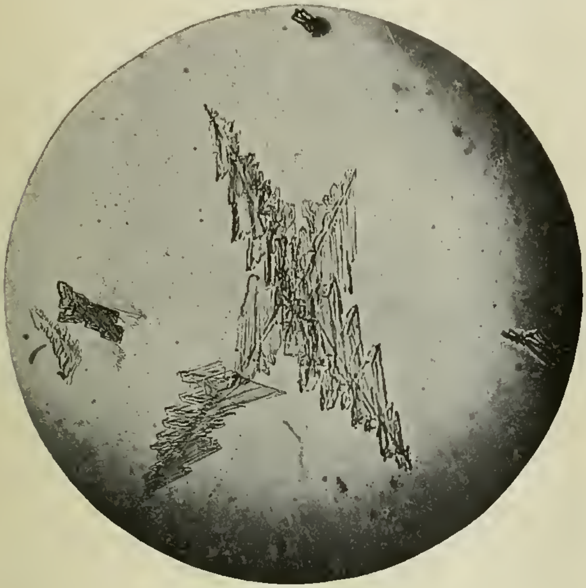

Fig. 2—Crystals of Silver Picrate-Mono-Cyanoguanidine Precipitated in the Presence of Fertilizer Materials. Magnified 120 Diameters

MICROSCOPIC APPEARANCE OF THE CRYSTALS—When silver picrate-mono-cyanoguanidine is formed as a gel and then allowed to crystallize, the crystals when viewed under the microscope (low power, magnification about 100 diameters) appear as in Fig. 1. They are almost perfect in form and appear to be very thin in one dimension. The exposed surface has the appearance of a slightly oblique parallelogram with four lines drawn from the four corners which meet at a point at the center. These lines are very distinct and seem to be the axes of the crystal since in imperfectly formed crystals they still persist. When the solution is stirred vigorously, causing direct precipitation of the crystals without passing through the gel stage, the resulting crystals are smaller but have the same general appearance as shown in Fig. 1, although considerable twinning is in evidence.

Certain compounds which are usually present when mixed fertilizers are analyzed cause a rather striking modification of the crystals.

Twelve grams of acid phosphate fertilizer were suspended in 100 cc. of water, and to this were added 100 cc. of a saturated solution of barium nitrate, and then a saturated solution of barium hydroxide, until the mixture was alkaline to litmus. This mixture was stirred for half an hour, made up to 500 cc., and filtered. Fifty cc. of this solution were made slightly acid with dilute nitric acid and treated with 5 cc. of a solution of dicyanodiamide (containing 21.0 mg.), 7 cc. of a 5 per cent silver nitrate solution, and 50 cc. of a saturated solution of picric acid. The beaker was left in an ice-water bath for 30 min., being stirred very gently once or twice during this period. Large crystals formed, a photomicrograph of which is shown in Fig. 2. An examination will show that the four lines shown in the crystals of Fig. 1 still persist, but that along two of the lines a great deal of twinning has taken place, resulting in these very striking "phantom crystals." The weight of the crystals was found to be 0.1054 g., corresponding to 21.1 mg. of dicyanodiamide, and this, together with their behavior when subjected to a melting-point determination, showed that they were identical with the crystals of Fig. 1.

A second experiment was carried out as above, except that 2 g. of ammonium sulfate were added to the acid phosphate, and the dicyanodiamide (0.2 g.) was added in the solid state, the mixture then being treated with water, barium nitrate, etc. These crystals, shown in Fig. 3,[1] were found to be identical with those already described.

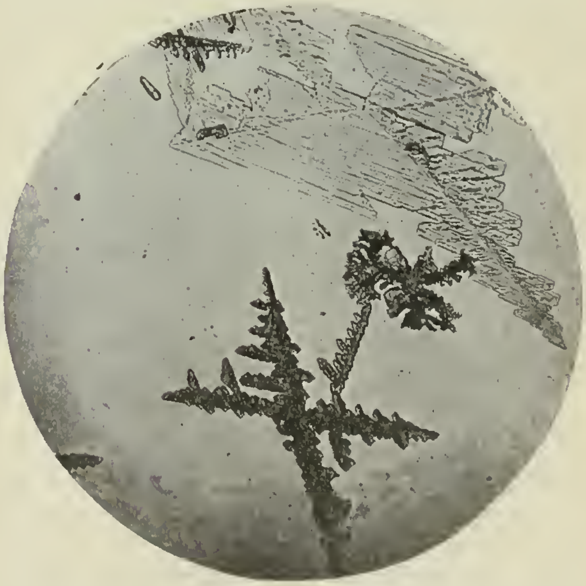

Fig. 3—Crystals of Silver Picrate-Mono-Cyanoguanidine Precipitated in the Presence of Fertilizer Materials Containing Ammonium Salts. Magnified 120 Diameters

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[1] The author is indebted to Mr. G. L. Keenan of the Microchemical Laboratory, Bureau of Chemistry, for making the above photomicrographs.

SOLUBILITY OF SILVER PICRATE-MONO-CYANOGUANIDINE IN WATER AND IN A SATURATED SOLUTION OF SILVER PICRATE—One hundred cc. of a saturated aqueous solution of the silver compound were evaporated to dryness in a weighed dish. To each of two other 100-cc. portions were added 15 cc. of 5 per cent silver nitrate solution and 100 cc. of saturated picric acid solution. The beakers containing the solutions were cooled in ice water for 30 min. with occasional stirring. The precipitates were collected on weighed Gooch crucibles, washed with a little saturated solution of silver picrate-mono-cyanoguanidine and with a little ether, dried for 30 min. at 100°, and weighed.

The following results were obtained:

Solubility of compound in 100 cc. of water	0.1128 g.
Compound precipitated by the silver picrate solution	0.1028 g.
Compound precipitated by the silver picrate solution	0.1037 g.
Quantity remaining in solution	0.0095 g.
Quantity remaining in 100 cc	0.0044 g.

SILVER PICRATE-DI-CYANOGUANIDINE—This compound was prepared by precipitating a saturated solution of dicyanodiamide with silver nitrate and picric acid, and recrystallizing the resulting product twice from water. It formed long, silky needles of a dark yellow color, the solubilities of which in various solvents very much resembled those of the corresponding mono-compound.

	N	Ag
Found	30.51 30.43	21.53
Calculated for $C_6H_2(NO_2)_3OAg.2C_2H_4N_4$	30.55	21.39

METHOD OF ANALYSIS

REAGENTS. *Silver Nitrate*—A 5 per cent solution.

Picric Acid—A practically saturated solution (about 1 g. per 100 cc.) made by shaking an excess of the solid with water for a minute or two.

Silver picrate-mono-cyanoguanidine—A saturated solution contained in a wash bottle. Precipitates from former analyses can be used.

Ether—Also contained in a wash bottle.

In addition to the above, the analysis of mixed fertilizers requires saturated solutions of barium nitrate and of barium hydroxide.

PROCEDURE—Make the solution of dicyanodiamide slightly acid to litmus. To each 100 cc. of this solution add 15 cc. of the silver nitrate solution and 100 cc. of the saturated solution of picric acid. Stir vigorously two or three times during the first 2 min., rubbing the walls of the beaker with the stirring rod, to prevent the formation of gel. Place the beaker in ice water for 30 min. In case crystals are slow to appear it is well to repeat the stirring once or twice during the cooling. Filter the precipitate upon a weighed Gooch crucible. The pad of asbestos should be very thin because the large crystals are not at all difficult to retain on the filter. With a properly prepared pad the mixture can be filtered almost as fast as it can be poured into the crucible. Wash out the crystals adhering to the walls of the beaker with the saturated solution in the wash bottle. It is sometimes necessary to employ a "policeman." Wash the precipitate once or twice with a little ether, dry in the oven 30 min. at 100°, cool in the desiccator, and weigh. To the weight of the precipitate add 0.0044 g. for each 100 cc. of the solution from which the crystals were filtered. The weight divided by five gives the quantity of dicyanodiamide in the solution analyzed. Should the analysis show that the original solution contained more than 2 mg. of dicyanodiamide per cc., which would give a precipitate of over 0.5 g. for each 100 cc. of solution filtered, the results are probably too low, and the analysis should be repeated with a more dilute solution.

APPLICATION TO COMMERCIAL CALCIUM CYANAMIDE—From 5 to 10 g. of the substance should be weighed out and agitated with 300 cc. of water for one-half to one hour. Add dilute nitric acid until the mixture is slightly acid to litmus, and then 75 cc. of the 5 per cent silver nitrate. Make up to 500 cc. and filter. For the analysis use a 100 or 200 cc. aliquot part and proceed as described above, omitting further addition of silver nitrate. The silver nitrate is added here before the mixture is filtered because some samples of Cyanamid contain sufficient carbides and similar substances to give a precipitate with silver nitrate.

APPLICATION TO MIXED FERTILIZER—Weigh out 20 g. of material, add 50 cc. of water, and stir. Now add 100 cc. of the solution of barium nitrate and then barium hydroxide until the mixture reacts alkaline to litmus. Agitate for 30 min., preferably with a stirrer. If the mixture is now acid, add more barium hydroxide until it is again slightly alkaline. Make up to 500 cc. and filter through a fluted filter. Use a 200-cc. portion for the analysis, proceeding as described above. If chlorides are present it will be necessary to filter again after the addition of the silver nitrate, before proceeding with the addition of the picric acid. In case the mixed fertilizer is unusually high in potassium salts, it is possible that the method will cause the precipitation of potassium picrate. Such an occurrence will be easily evident from the long needles thrown down, and also from the fact that the ether used to wash the precipitate will be colored a bright yellow. In this case a more dilute solution of the sample should be employed. The presence of cottonseed meal interferes with the analysis, certain soluble materials from the meal forming a gelatinous precipitate with the picric acid. This can be avoided by adding 30 cc. of a 10 per cent lead acetate solution immediately after the addition of barium hydroxide. If this is done, it is necessary to add more nitric acid when the solution is acidified, as the presence of acetates tends to lower the H^+-ion concentration, and if cyanamide is present it will be precipitated when the silver nitrate is added. If silver cyanamide should appear, it can be redissolved by adding more nitric acid and the analysis carried out as usual.

RESULTS OF ANALYSES BY THE METHOD

PURE DICYANODIAMIDE—Samples of this compound were weighed out and dissolved in varying volumes of water and the analysis carried out as described above. The results are given in Table I. The last example, where the cyanamide content of the solution analyzed was 3.33 mg. per cc., shows that with this concentration of dicyanodiamide the results are somewhat too low.

TABLE I

Volume of Dicyanodiamide Solution Cc.	Weight of Dicyanodiamide Used Mg.	Weight of Dicyanodiamide Found Mg.
50	50.0	49.9
100	50.0	49.3
100	50.0	49.8
50	34.4	35.5
100	50.0	49.2
50	56.3	56.4
25	2.5	2.3
50	50.0	49.4
25	50.0	48.9
30	100.0	93.6

DICYANODIAMIDE AND CYANAMIDE—To a solution containing 100 mg. of cyanamide ($CNNH_2$) in 50 cc. there were added 41.8 mg. of pure dicyanodiamide. Two such solutions were analyzed. The analysis gave 41.9 mg. and 42.2 mg. dicyanodiamide. Similar analyses carried out with the cyanamide solution alone showed no dicyanodiamide.

DICYANODIAMIDE AND UREA—A solution, containing 50 mg. of urea and 20 mg. of dicyanodiamide in 50 cc. of water gave on analysis 19.5 mg. of dicyanodiamide. A solution of pure urea containing 4 mg. per cc. gave no precipitate at all with the reagents, and the same result was secured with a urea solution containing 100 mg. per cc.

DICYANODIAMIDE AND MIXED FERTILIZER MATERIALS—A mixture was prepared consisting of acid phosphate (12 g.), ammonium sulfate (4.2 g.), potassium sulfate (1.5 g.), and dried peat (4 g.). To this were added 50 cc. of water containing 81.2 g. of dicyanodiamide. The mixture was treated with barium nitrate, barium hydroxide, etc., and the analysis carried out as described above for mixed fertilizers. The results of duplicate analyses were 81.5 and 81.5 mg. of dicyanodiamide.

A somewhat similar analysis has already been reported in one of the experiments under the heading of "microscopic appearance of the crystals."

THE CHANGES TAKING PLACE IN CYANAMID WHEN MIXED WITH FERTILIZER MATERIALS[1]

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In an attempt to analyze an aqueous extract of a mixed fertilizer for cyanamide by the method of Perotti,[2] it was found that the presence of phosphates interfered, since they, too, formed a precipitate with the silver nitrate upon making the solution alkaline with ammonium hydroxide. The difficulty was overcome by precipitating the phosphates by means of barium hydroxide and analyzing the filtrate. Although the manufacturer stated that the fertilizer contained considerable quantities of cyanamide, not even a trace was found. To test the accuracy of the method a mixed fertilizer was prepared containing a known weight of calcium cyanamide (Cyanamid) whose cyanamide content was known. The accurate results obtained upon analysis showed that the method was applicable. Some days later a second sample of this mixture was analyzed, and to our surprise it was found that all the cyanamide had disappeared. Another fertilizer mixture was now prepared, its composition being identical with the previous one, and at intervals over a period of two weeks samples were withdrawn and analyzed for cyanamide. The loss of cyanamide was very rapid, 60 per cent having disappeared in 24 hrs., and within 10 days it had practically all vanished. This at once suggested an investigation to determine, first, the cause of this rapid disappearance of cyanamide, and, second, the products resulting from the transformation.

A search through the literature showed that while a vast amount of work has been done in reference to the changes taking place when Cyanamid alone is added to the soil or is kept in storage, and that while studies have been made in regard to the changes occurring in the soluble phosphates of mixed fertilizer containing Cyanamid, it is a curious fact that no one seems to have paid any attention to the changes which may occur in cyanamide when this extremely reactive substance is mixed with other fertilizer materials. The present paper reports some results of such an investigation.

FACTORS CAUSING TRANSFORMATION OF CYANAMIDE

The fertilizer mixture which was prepared was composed of acid phosphate, ammonium sulfate, potassium sulfate, and Cyanamid (all being the usual commercial products), and dried peat. In order to ascertain which of these materials was instrumental in bringing about the rapid disappearance of cyanamide, mixtures containing Cyanamid and various combinations of these substances were prepared. Since it seemed probable that the acid phosphate was involved in the reaction it was used in each of the mixtures. The mixtures were: (1) acid phosphate and Cyanamid; (2) potassium sulfate, acid phosphate, and Cyanamid; (3) ammonium sulfate, acid phosphate, and Cyanamid; and (4) dried peat, acid phosphate, and Cyanamid. Samples from these mixtures were analyzed at intervals. While all of the mixtures caused a slight decrease in cyanamide, only Mixture 4 showed any considerable decrease, the rate here being rapid and practically parallel to that of the original mixture. This suggested that perhaps the dried peat was not so dry as the name would indicate, and an analysis of this material showed that it did contain 36 per cent of moisture. The other materials were practically dry, although the acid phosphate contained a little moisture. In a mixture containing acid phosphate, Cyanamid, and 8 per cent of water, the cyanamide decreased very rapidly, only 5 per cent of it remaining at the end of 3 days. Several similar mixtures exhibited this same rapid decrease in cyanamide content. To test the effect of moisture alone, moist quartz containing 10 per cent of water was mixed with Cyanamid. Here, too, there was a decrease in cyanamide, resulting finally in its disappearance, but the rate was by no means so rapid as when moist acid phosphate was employed, the loss of cyanamide in the latter mixture during the first day being eight times as great as that in the moist quartz mixture. On the other hand,

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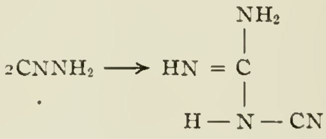
[1] Presented at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

[2] *Rend. soc. chim. ital.*, **1904**, 192.

Cyanamid when mixed with practically dry acid phosphate remained unchanged even after 2 or 3 mo. This rapid disappearance of cyanamide must therefore be caused by the presence of acid phosphate and a small amount of moisture. This conclusion was further confirmed by experiments with complete mixed fertilizer, since only those samples in which these conditions existed (*i. e.*, acid phosphate and 5 to 10 per cent of moisture) showed any considerable decrease in cyanamide.

CHEMICAL CHANGES INVOLVED

Upon complete evaporation of a sample from one of the mixed fertilizers, the cyanamide of which had entirely disappeared, there was left a quantity of long needles, which were identified as dicyanodiamide by the method described in the preceding paper. A quantitative determination of dicyanodiamide, made upon another sample of this fertilizer, showed that 90 per cent of the cyanamide originally present had been transformed into dicyanodiamide. The mixture had now stood 30 days. At the end of 100 days it was again analyzed, and the results showed that the dicyanodiamide content was practically unchanged. Another mixture of Cyanamid and acid phosphate, containing about 10 per cent of moisture, was next prepared, and the changes taking place in cyanamide and dicyanodiamide content were followed by making simultaneous analyses for these two substances at intervals. Since the chemical change occurring in the formation of dicyanodiamide from cyanamide is simply the union of two molecules of cyanamide to form a molecule of dicyanodiamide, according to the equation



$$2CNNH_2 \longrightarrow \begin{array}{rcl} & NH_2 & \\ & | & \\ HN = & C & \\ & | & \\ H- & N & -CN \end{array}$$

there is no alteration in weight, and if this reaction is the only one involved the weight of dicyanodiamide produced should equal that of the cyanamide lost; or, stated differently, the combined weights of cyanamide and dicyanodiamide should remain constant. This study served to confirm what was apparent from the results already secured: namely, that in the disappearance of cyanamide the principal chemical change was the formation of dicyanodiamide, and that under the conditions employed this was at all times practically quantitative. A similar study conducted with two complete mixed fertilizers yielded practically the same results, although toward the end of the period the amount of dicyanodiamide in the mixture did not so closely approximate the quantity of cyanamide which had disappeared, the final yield of dicyanodiamide representing only about 65 per cent of the loss in cyanamide. Whether this result was due to a parallel reaction which produced some other compound from the cyanamide—possibly urea—or whether part of the dicyanodiamide formed was subsequently decomposed into other compounds, has not yet been determined.

When Cyanamid and moist acid phosphate (6 to 10 per cent H_2O) were mixed, with or without other fertilizer materials, a rise in temperature of 20° to 30° C. was always observed, and the mixture set to a hard mass upon standing. When analyzed immediately there was no loss of cyanamide. The acid phosphate possessed but slight acidity, 10 g. of this material requiring 27.5 cc. of 0.1 *N* alkali to titrate to the neutral point with methyl red; yet when 1 g. of Cyanamid, which required 169 cc. of 0.1 *N* sulfuric acid to reach the same end-point, was added to 10 g. of moist acid phosphate, the resulting mixture, when added to water, was always acid to litmus. An alkaline mixture could be obtained only by adding a considerably larger quantity of Cyanamid. This can only mean an interaction between the acid phosphate and Cyanamid. de Nolinari and Ligot[1] and later Brackett[2] showed that when Cyanamid and acid phosphate were mixed there resulted a "reversion" of the phosphate, *i. e.*, the introduction of more calcium into the acid phosphate molecule to form insoluble phosphates. When these facts are considered together, they indicate the probable course of the reaction which results in the rapid loss of cyanamide. The calcium cyanamide and acid phosphate first react to form dicalcium or tricalcium phosphate and free cyanamide:

$$2Ca{:}NCN + CaH_4(PO_4)_2 \longrightarrow 2CaHPO_4 + CNNH_2$$
$$Ca{:}NCN + 2CaHPO_4 \longrightarrow Ca_3(PO_4)_2 + CNNH_2$$

and the free cyanamide thus produced is rapidly transformed into dicyanodiamide and other products.

Up to this point in the investigation, the fertilizer mixtures contained less than 1 part of Cyanamid to 10 parts of acid phosphate. In a mixture of moist acid phosphate and Cyanamid, containing 25 per cent of Cyanamid, there was also a rapid conversion to dicyanodiamide (practically quantitative), but only about 60 per cent of the cyanamide was thus transformed, and after this point was reached very little further change resulted. It is evident, therefore, that there is a limit to the quantity of cyanamide which a given quantity of moist acid phosphate will transform.

Reference has already been made to the fact that the mixing of Cyanamid with moist quartz caused a disappearance of cyanamide. It was found that most of the cyanamide was changed into dicyanodiamide. That this change would take place was somewhat to be expected, since Perotti[3] and Hager and Kern[4] have shown that when Cyanamid containing moisture was stored for several months a large portion of the cyanamide was converted into dicyanodiamide.

Finally, analyses were made of six samples of mixed fertilizer, containing varying amounts of Cyanamid, which had been prepared for certain 1920 field tests carried out by the Division.[5] Four weeks had elapsed since the fertilizers had been mixed. Each sample was found to contain a large quantity of dicyanodiamide, the amounts of this compound ranging from 11.4 to 33.4 lbs. per ton of the fertilizer mixtures.

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[1] *J. soc. agr. Brabant et Hainant*, **54** (1909), 161.

[2] THIS JOURNAL, **5** (1913), 933.

[3] *Atti acad. Lincei*, [5] **15** (1906), I, 48.

[4] *Z. angew. Chem.*, **29** (1916), 221.

[5] Prepared for field tests in experimental work being conducted by Dr. O. Schreiner, Dr. J. J. Skinner, and Mr. B. E. Brown, of Soil Fertility Investigations. The mixtures were prepared according to the usual fertilizer practice, no modifications being introduced, with a view of studying any changes in the cyanamide content.

EXPERIMENTAL DETAILS

MATERIALS EMPLOYED. *Acid Phosphate*—This was the usual type of fertilizer material, containing 16 per cent of available P_2O_5.

Ammonium Sulfate—The crude material of commerce, containing 25 per cent of NH_3.

Potassium Sulfate—The salt commonly used in fertilizer, containing 50 per cent of K_2O.

Cyanamid—This was technical calcium cyanamide, a hydrated material which was about a year old and contained 21 per cent of cyanamide and 2.3 per cent of dicyanodiamide. In two of the experiments, there was used a more recently purchased hydrated Cyanamid which contained 29.4 per cent of cyanamide and no dicyanodiamide.

METHODS OF ANALYSIS—A 20 g. sample (in mixtures containing more than 6 per cent of Cyanamid, a 10 g. sample was used) of the fertilizer mixture was stirred with 50 cc. of water. To this were added 100 cc. of a saturated solution of barium nitrate and then a solution of barium hydroxide until the mixture was slightly alkaline to litmus. The barium hydroxide was added to precipitate phosphates, but when ammonium sulfate was present this would have produced large amounts of ammonium hydroxide, which would convert some of the cyanamide to dicyanodiamide. The barium nitrate was therefore added to prevent this ammonia formation. The mixture was agitated vigorously for 30 min. with a mechanical stirrer, then transferred to a 500 cc. graduated flask, made up to the mark, thoroughly mixed, and filtered. Two 200 cc. portions were measured out, and one was analyzed for cyanamide and the other for dicyanodiamide. To determine cyanamide the method of Perotti, as modified by Brioux,[1] was employed, the precipitate of silver cyanamide being dissolved in dilute nitric acid and titrated against 0.1 *N* ammonium thiocyanate solution. For the determination of dicyanodiamide the method described in the preceding paper was used.

CHANGES IN CYANAMIDE CONTENT OF A MIXED FERTILIZER

Fertilizer Mixture A contained:

	Grams
Acid phosphate	100
Potassium sulfate	12
Ammonium sulfate	42
Cyanamid	10
Dried peat	36
Total	200

The materials were ground together in a mortar until they would pass through a 20-mesh sieve, and further mixed on a large piece of glazed paper. The mixture was analyzed immediately for cyanamide, and the analysis was repeated at intervals for 13 days, with the results given in Table I and shown graphically in Fig. 1.

TABLE I—CHANGES IN CYANAMIDE CONTENT OF A COMPLETE MIXED FERTILIZER (MIXTURE A)

Time Days	Mg. Cyanamide per G. Cyanamid Used
Immediately after mixing	220.0
1	95.5
3	75.6
4	46.2
6	41.1
13	23.1

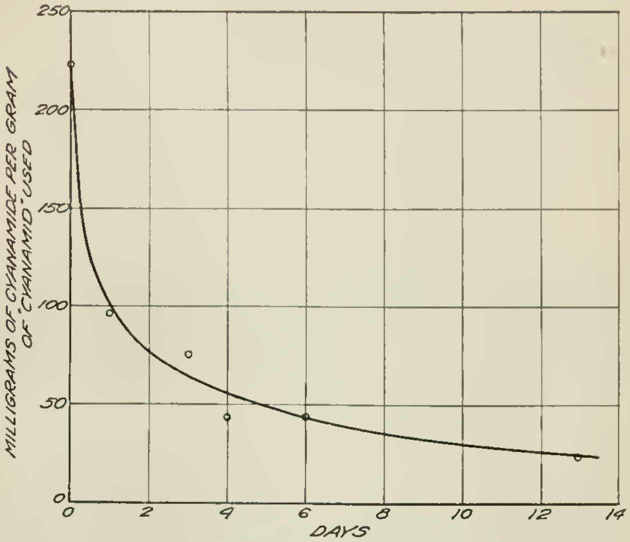

FIG. 1—CHANGES IN CYANAMIDE CONTENT OF A COMPLETE MIXED FERTILIZER CONTAINING "CYANAMID"

INFLUENCE OF VARIOUS FERTILIZER INGREDIENTS

Four mixtures were prepared containing various combinations of Cyanamid with the other materials used in the previous experiments, as follows:

(*a*)	Grams
Acid phosphate	90
Cyanamid	10

(*b*)	Grams
Acid phosphate	45
Ammonium sulfate	18
Cyanamid	5.5

(*c*)	
Acid phosphate	45
Potassium sulfate	6
Cyanamid	5

(*d*)	
Acid phosphate	45
Dried peat	18
Cyanamid	5.5

The results of analyses are given in Table II.

TABLE II—CHANGES IN CYANAMIDE CONTENT OF VARIOUS MIXTURES OF "CYANAMID" AND ACID PHOSPHATE WITH OTHER FERTILIZER MATERIALS

Time Days	Mg. Cyanamide per G. Cyanamid Used			
	(*a*)	(*b*)	(*c*)	(*d*)
Immediately after mixing	202	196	210	201
1	180	152	192	...
2	164	...	...	94
4	...	...	...	82
5	...	139	...	...
9	120	...	190	...

EFFECT OF MOISTURE CONTENT OF FERTILIZER MATERIALS

Moisture in the materials was determined by drying for 20 hrs. at 100° C.

	H_2O Per cent
Ammonium sulfate	0.4
Potassium sulfate	0.18
Dried peat	36.0
Acid phosphate	2.7

In the experiments described above the acid phosphate probably contained slightly more than 2.7 per cent of moisture since some weeks elapsed before the moisture content was determined, and during this time it had been stored in a paper bag exposed to the drying action of the air. At the time the experiments were performed the acid phosphate had already been considerably air-dried, so it contained much less moisture than fresh acid phosphate, the moisture content of the latter being 6 to 10 per cent.

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[1] *Ann. chim. anal.*, **15** (1910), 341.

I—CHANGES IN CYANAMIDE CONTENT

CYANAMID AND MOIST ACID PHOSPHATE—Mixture B was prepared containing:

Acid phosphate (2.7 per cent H_2O), grams	82
Cyanamid, grams	10
Water, grams	8
Total moisture, per cent	10.2

The water was added to the acid phosphate and the material ground in the mortar until uniform, the resulting mixture appearing quite moist. The Cyanamid was now added and this mixture again made uniform by grinding. Almost at once all evidence of moisture disappeared, and a fine, dry powder resulted. During this change, the temperature rose from 24° to 45° C. When the resulting mixture was added to water it showed a strongly acid reaction toward litmus. The mixture was analyzed for cyanamide immediately and at intervals over a period of 6 days, the results being given in Table III.

TABLE III—CHANGES IN CYANAMIDE CONTENT OF A MIXTURE OF "CYANAMID" AND MOIST ACID PHOSPHATE (MIXTURE B)

TIME	Mg. of Cyanamide per G. of Cyanamid Used
0 hrs.	210
5 hrs.	97.6
2 days	21.4
6 days	17.3

CYANAMID AND AIR-DRY ACID PHOSPHATE—Mixture C contained:

Acid phosphate (2.7 per cent H_2O), grams	90
Cyanamid, grams	10
Total moisture, per cent	2.2

and was mixed as in the preceding experiment. Immediately after mixing it contained 223 mg. of cyanamide per gram of Cyanamid, and after standing 18 days it was found to contain 194 mg. per gram of Cyanamid used.

CYANAMID AND MOIST QUARTZ—A mixture, D, containing

Quartz (ground to 200 mesh), grams	90
Water, grams	10
Cyanamid, grams	11.1
Total moisture, per cent	9

was prepared and analyzed as in the previous experiments. There was no rise in temperature when the mixture was prepared, and it remained moist, clinging together like moist sand when the jar containing it was rotated. After a day an odor of ammonia was given off. At the end of 2 wks. it was somewhat more dry, but the particles still clung together, and it was by no means the dry powder described in the experiment with moist acid phosphate. Table IV gives the results of analyses of this material.

TABLE IV—CHANGES IN CYANAMIDE CONTENT OF A MIXTURE OF "CYANAMID" AND MOIST QUARTZ (MIXTURE D)

TIME	Mg. of Cyanamide per G. of Cyanamid Used
0 hrs.	213.6
24 hrs.	185.8
2 days	131.25
9 days	31.5

The results for Mixtures B, C, and D are shown graphically in Fig. 2.

AVAILABLE ACID IN ACID PHOSPHATE—One gram of acid phosphate was extracted for 0.5 hr. with 500 cc. of water. The filtrate was strongly acid to litmus. Upon titration against 0.1 *N* sodium hydroxide, using methyl red as an indicator, 2.75 cc. of the alkali were required.

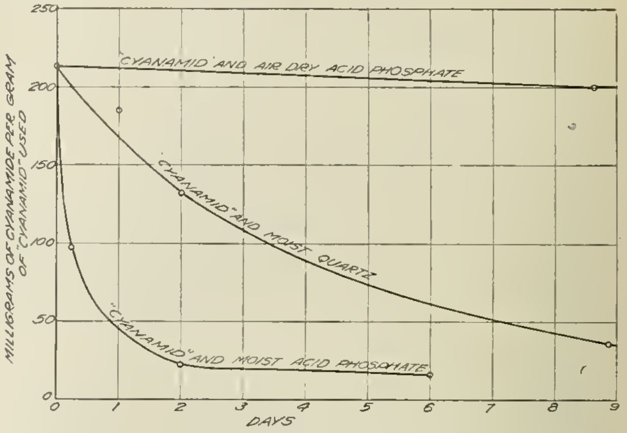

FIG. 2—CHANGES IN CYANAMIDE CONTENT OF "CYANAMID" WHEN MIXED WITH AIR-DRY ACID PHOSPHATE, MOIST ACID PHOSPHATE, AND MOIST QUARTZ

AVAILABLE ALKALI IN CYANAMID—One gram of the Cyanamid was stirred vigorously with 500 cc. of water for 30 min., and filtered. The filtrate, which was strongly alkaline to litmus, required 169 cc. of 0.1 *N* sulfuric acid for neutralization with methyl red as indicator.

DICYANODIAMIDE CONTENT OF THE MIXTURES—Twenty grams of Mixture B were stirred for 30 min. with 200 cc. of absolute acetone, and filtered. The acetone extract was evaporated to dryness, leaving a quantity of long needles mixed with some dark material. Recrystallization of the residue from water gave colorless needles, melting at 205°, whose melting point was unchanged when mixed with dicyanodiamide. A solution of these crystals gave yellow crystals of silver picrate monocyanoguanidine (m. p. 230°) upon treatment with picric acid and silver nitrate (Fig. 1, preceding paper). A quantitative determination of dicyanodiamide in Mixture B gave 179 mg. of dicyanodiamide per gram of Cyanamid, at the end of 4 wks. At the end of 15 wks., the mixture contained 193.5 mg. of dicyanodiamide per gram of Cyanamid used. Mixture C contained but 7.9 mg. of dicyanodiamide per gram of Cyanamid. Mixture D at the end of 9 days contained 171.2 mg. of dicyanodiamide per gram of Cyanamid used. A quantitative conversion of the cyanamide to dicyanodiamide would have required the appearance of 230 mg. of dicyanodiamide per gram of Cyanamid used.

II—SIMULTANEOUS CHANGES IN CYANAMIDE AND DICYANODIAMIDE CONTENT

CYANAMID AND MOIST ACID PHOSPHATE—The following Mixture E was prepared:

Acid phosphate (2.7 per cent H_2O), grams	184
Water, grams	16
Cyanamid, grams	22.2
Total moisture per cent	10.2

Analyses for cyanamide and dicyanodiamide were made immediately, and at intervals over a period of 8 days. The results are shown in Table V and Fig. 3.

Table V—Simultaneous Changes in Cyanamide and Dicyanodiamide in a Mixture of "Cyanamid" and Moist Acid Phosphate (Mixture E)

Time	Cyanamide (Mg. per G. of Cyanamid Used)	Dicyanodiamide (Mg. per G. of Cyanamid Used)
0 hrs.	208.9	13.5
5 hrs.	130.0	113.2
28 hrs.	75.6	175.8
2 days	49.8	184.6
5 days	44.6	180.2
8 days	30.5	182.4

The above experiment was twice repeated with practically identical results.

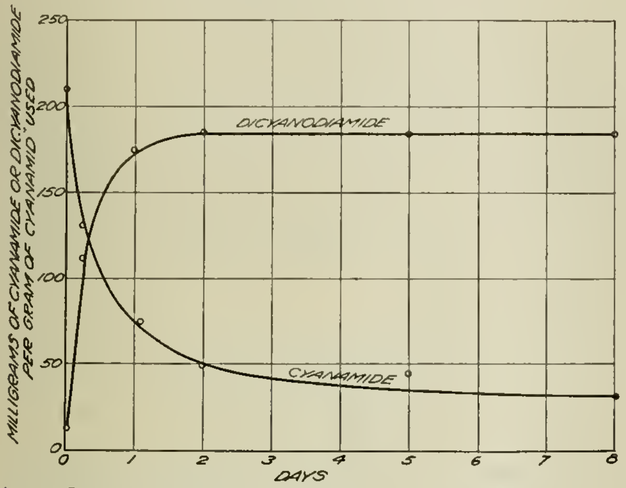

Fig. 3—Simultaneous Disappearance of Cyanamide and Formation of Dicyanodiamide in a Mixture of "Cyanamid" and Acid Phosphate

MOIST ACID PHOSPHATE AND EXCESS OF CYANAMID—Mixture F was prepared and studied in the usual way. The Cyanamid used was the more recently purchased sample containing 29.4 per cent of cyanamide. This mixture, when added to water, was alkaline to litmus.

Acid phosphate (2.7 per cent H_2O), grams	67
Water, grams	8
Cyanamid, grams	25
Total moisture, per cent	9.8

Table VI gives the results.

Table VI—Simultaneous Changes in Cyanamide and Dicyanodiamide in a Mixture of Moist Acid Phosphate and an Excess of "Cyanamid" (Mixture F)

Time	Cyanamide (Mg. per G. of Cyanamid Used)	Dicyanodiamide (Mg. per G. of Cyanamid Used)
0 hrs.	277	0
2 days	191	97
8 days	155	122
41 days	127	142

CYANAMID IN COMPLETE FERTILIZER MIXTURES—Three complete fertilizer mixtures were prepared, their composition being:

	(Mixtures G and H)	(Mixture I)
Acid phosphate (2.7 per cent H_2O), grams	200	200
Potassium sulfate, grams	24	24
Ammonium sulfate, grams	84	84
Dried peat (9 per cent H_2O), grams	42	72
Water, grams	30	..
Cyanamid, grams	20	20
Total moisture, per cent	9.8	3.2

Mixtures G and I were prepared by grinding in the mortar. Since in actual fertilizer practice the materials are merely mixed with a shovel, Mixture H was mixed by means of a spatula. The results are given in Table VII.

Table VII—Simultaneous Changes in Cyanamide and Dicyanodiamide Content of Three Complete Mixed Fertilizers

Time	Cyanamide (Mg. per G. of Cyanamid Used) G	H	I	Dicyanodiamide (Mg. per G. of Cyanamid Used) G	H	I
0 hrs.	223	221	210	14	10	...
1 day	143	128	...	86	100	...
3 days	102	67	201	111	126	...
15 days	...	...	199	...	...	...
18 days	14	9	...	104	136	...
34 days	...	5	201	98	136	...

DICYANODIAMIDE CONTENT OF MIXED FERTILIZERS—Six mixed fertilizers which had been prepared for use in the field tests of this Department were analyzed for cyanamide and dicyanodiamide. The compositions of the mixtures were as follows:

Ingredients	Mixture, Weight in Pounds (1)	(2)	(3)	(4)	(5)	(6)
Sodium nitrate	4.5	4.5	6.8	2.3	..	..
Ammonium sulfate	3.4	..	..	..	..	4
Dried blood	..	5.3	8.4	2.7	10.7	..
Acid phosphate	42.7	42.7	42.7	42.7	42.7	25
Potassium sulfate	13.6	13.6	13.6	13.6	13.6	4
Cyanamid	7.8	7.8	3.9	7.8	7.8	8
Sand (air-dry)	25.7	25.8	22.3	22.9	22.9	9
Total	97.7	99.7	97.7	97.6	97.7	50

The Cyanamid used in the first five mixtures was 2 yrs. old and contained 15.4 per cent of cyanamide and 6.2 per cent of dicyanodiamide. For Mixture 6 there was used the more recently purchased Cyanamid containing 29.4 per cent of cyanamide. The results are given in Table VIII.

Table VIII—Cyanamide and Dicyanodiamide Content of 20 Grams of Complete Fertilizer Mixtures when Mixed and Five Weeks Afterward

Mixture	Cyanamide Added Mg.	Cyanamide Found after 5 Wks. Mg.	Dicyanodiamide Added Mg.	Dicyanodiamide Found after 5 Wks. Mg.
1	240	89	99	214
2	240	106	99	211
3	120	40	50	114
4	320	171	132	249
5	240	142	99	201
6	940	648	...	334

EFFECT OF USING SMALLER PROPORTIONS OF CYANAMID—Four mixtures of moist acid phosphate and Cyanamid were prepared, containing in each 1000 g. of mixture 25, 50, 75, and 100 g., respectively, of Cyanamid. Since mixed fertilizers commonly contain about 50 per cent of acid phosphate, these mixtures would correspond to 25, 50, 75, and 100 lbs. of Cyanamid per ton of mixed fertilizer. They were prepared as in the previous experiments, using another supply of acid phosphate containing 3 per cent of moisture, to which was added water so that all mixtures contained practically 10 per cent of moisture, to approximate the moisture condition of commercial acid phosphate. In the three lower concentrations of Cyanamid duplicate mixtures were prepared, using for comparison the acid phosphate employed in the previous experiments.

After 3 days the mixtures were analyzed for cyanamide and dicyanodiamide, with the results given in Table IX.

Table IX—Changes Taking Place in 20 Grams of Mixtures of Moist Acid Phosphate with Varying Amounts of "Cyanamid"

Parts Cyanamid in 1000 Parts Mixture	When Mixed Cyanamide Mg.	After 3 Days Cyanamide Mg.	After 3 Days Dicyanodiamide Mg.
25	145	99	6
25	145	29	7
50	290	97	91
50	290	85	74
50	290	66	125
75	435	61	348
75	435	44	353
100	580	32	498

It will be noticed that while the formation of dicyanodiamide is less with the smaller quantities of Cyanamid used in the fertilizer, yet the change to dicyanodiamide is still very considerable with 50 lbs. per ton.

CONCLUSIONS

Further investigations are being conducted, but the results already secured seem to warrant the following conclusions, at least in so far as the conditions of concentration, temperature, and moisture here reported on are concerned:

1—When Cyanamid is mixed with fertilizer materials containing acid phosphate and 5 to 10 per cent of moisture, the cyanamide content decreases with great rapidity.

2—This change is represented partially by, and in the higher concentrations principally by, the formation of dicyanodiamide.

3—A given quantity of moist acid phosphate is able to transform a limited amount of calcium cyanamide.

4—Cyanamid is not affected by dry acid phosphate.

5—Moisture alone is able to cause the conversion of cyanamide to dicyanodiamide, but the change is much slower than when acid phosphate is present.

Since it has been repeatedly shown that dicyanodiamide is valueless as a fertilizer material, and, moreover, is toxic to many plants,[1] the formation of this compound in fertilizer materials seems undesirable. On first thought, it would appear that this conversion of cyanamide into dicyanodiamide could be avoided by employing dry fertilizer mixtures, but this overlooks the fact that when such mixtures are added to the soil, moisture conditions are at once provided, and the transformation may possibly then take place. Preliminary experiments carried out in this laboratory indicate that, under certain conditions at least, this is the case.

It should be noted that these unfortunate reactions between acid phosphate and Cyanamid do not in any sense imply that Cyanamid cannot be successfully used when mixed with other forms of phosphate. In this connection it should be noted that the Fixed Nitrogen Research Laboratory of the Ordnance Department has called our attention to the fact that lime nitrogen (Cyanamid) can be mixed with calcined and basic phosphates without the excessive production of dicyanodiamide noted when moist acid phosphate is used.

STUDIES ON THE CORROSIVE ACTION OF CHLORINE-TREATED WATER. I—THE EFFECTS OF STEEL ON THE EQUILIBRIUM: $Cl_2 + H_2O \rightleftharpoons HCl + HClO$, AND OF PRODUCTS OF THE EQUILIBRIUM ON STEEL

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Vanderbilt University, Nashville, Tennessee

Received July 17, 1920

In the entire range of the subject matter of chemistry there is scarcely a phase upon which more work has been done, and concerning which there is greater deviation of opinion expressed in the literature, than upon solutions of chlorine gas in water. The importance of a thorough knowledge of such solutions lies in the fact that so many distinct fields are concerned. The physical chemist is interested in all phases of the equilibrium established between the products of the reaction

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl$$

and how this may affect the properties of each substance. The bacteriologist and sanitary engineer are concerned with the amount of chlorine it is necessary to add to natural waters in order to render them potable. The physiologist is interested in discovering the effect upon bodily functions and metabolism of the introduction of chlorine-treated water into the alimentary canal. The fields of the engineer and metallurgist converge in considering the effect of chlorine water upon the corrosion of iron and steel pipes and upon steam boilers.

Applications of this problem have been widely recognized, as is indicated by the numerous papers to be found touching in varying fashion upon some phase of the subject. There are two outstanding facts to be gained from a survey of the literature: first, the extremely qualitative nature of the great majority of these reported observations; and hence, second, the wide differences of opinion, even to the point of diametrical opposition, on some of the most fundamental points of the chemistry, corrosive effects, and physiological action. It is not within the scope of this paper to undertake any extensive critique of the work which has been done; the work which may be considered most authoritative will be referred to later. With these large discrepancies and rather serious omissions in the present knowledge of the solution of chlorine in water clearly in mind, this series of researches has been undertaken with the ostensible purpose of attempting to bring order out of an indefinite and unsatisfactory state of a scientific subject, with especial reference to the application to the city water supply of Nashville, Tennessee.

Of course, of the greatest importance from any standpoint is the question whether or not city water which has been treated with chlorine is physiologically injurious when used for drinking purposes. There is not to be found in the literature a record of any complete biological research of this kind, though work upon the effect of chlorine gas in respiratory processes is extensive and conclusive since the war. There is an almost even division of opinion among medical men as to whether chlorine-treated water is, or is not, injurious in metabolism. One writer finds it beneficial in the treatment of such diseases as infantile diarrhea, and another argues that even very slight traces are injurious to the organism. There must be established, therefore, by careful research upon living organisms just what the effect of chlorine-treated water is, and what the maximum allowable concentration of the gas may be without serious consequences.

Before any adequate interpretation of such experiments can be made, however, it is necessary to know exactly the chemistry involved—the compounds formed, and their concentration, activity, and relation to each other, when chlorine is dissolved in water. This paper is, therefore, preliminary to more practical work on the corrosive action upon living organisms and upon metal containers and pipes,[1] the cause and nature of which may then be adequately and scientifically explained. It involves essentially a study of the reaction between chlorine and water to form hydrochloric and hypochlorous acids; the determination of equilibrium conditions and the disturbing of them by time, light, and the presence of steel, alkali, and excess products; methods of analysis of the products in the presence of each other; the effect upon the passive state and the corrosion of steel; the settling of the controversy concerning the existence of "fixed chlorine;" and a study of some new oxidizing properties of the solution of chlorine in water.

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[1] Brioux, *Ann. Sci. Agron.*, [3] **1** (1910), 241; Hovermann and Koch, *J. Landw.*, **64** (1916), 317; Pfeiffer and Simmermacher, *Landw. Vers.-Sta.*, **90** (1917), 415; Johnson, *Tid. Kemi, Farm. Terapi*, **15** (1918), 349; Cowie, *J. Agr. Sci.*, **9** (1919), 113.

The work to be described may be subdivided into the following heads:

(*a*) The solution of chlorine in water:
    Methods of analysis
    Equilibrium in the system
    Effect of iron on equilibrium
    Interpretation of results
(*b*) Corrosion of iron and steel:
    Nature, and extent
    Interpretation
    Secondary effects

THE SYSTEM Cl_2–H_2O–HOCl–HCl

It has been long known that when the reaction

$$Cl_2 + H_2O \rightleftarrows HCl + HClO$$

takes place out of contact of light and in the cold, equilibrium is established. There is, however, very great disagreement as to the exact conditions and concentrations which determine the equilibrium, and the constant has never been determined. Much better known is the action of sunlight upon chlorine water, in which the following monomolecular reaction proceeds:

$$2HOCl \rightleftarrows 2HCl + O_2$$

Also well known is the extensive work on the reaction comprising the Deacon process

$$2H_2O + 2Cl_2 \rightleftarrows O_2 + 4HCl$$

which is carried out at high temperatures in the presence of bricks soaked with $CuCl_2$ as catalyst. The equilibrium constant is about 2.4 at 430°.

A fourth equilibrium is the following:

$$3H_2O + 3Cl_2 \rightleftarrows HClO_3 + 5HCl$$

which has been fully investigated by Sands,[2] Foerster,[3] Luther and McDougall,[4] and Olson.[5] The latter determined an equilibrium constant of 4.3×10^{-7} at 364° Å., and also found that the effect of hastening to equilibrium with iron as catalyst was unsatisfactory.

ANALYTICAL METHODS

Perhaps the greatest difficulty in establishing definite relationships in the first of the four above equations, with which this entire series of studies is concerned, is to be found in a method of analysis by which it would be possible to determine chlorine, and both hypochlorous and hydrochloric acids, in the presence of each other. The usual method for thus determining chlorine and hypochlorous acid in the presence of each other takes hydrochloric acid into account not at all, and thus introduces large errors. The determination is based upon the following reactions:

$$HOCl + 2NaI \rightleftarrows NaCl + NaOH + I_2$$
$$Cl_2 + 2NaI \rightleftarrows 2NaCl + I_2$$

One mole of HOCl sets free one mole of I_2 and produces at the same time one mole of NaOH, while the chlorine simply sets free an equivalent amount of iodine. After neutralizing the alkali with an excess of hydrochloric acid and determining the iodine by titration with sodium thiosulfate, the excess of hydrochloric acid is titrated with standard alkali solution. The NaOH produced by the action of hypochlorous acid upon the iodide obviously requires half as much of, say, 0.01 *N* acid, for neutralization as is required of 0.01 *N* $Na_2S_2O_3$ solution to react with the iodine set free by the action of the hypochlorous acid. From this is calculated how much of the $Na_2S_2O_3$ is required for the free chlorine. It is clear, therefore, that this method depends entirely upon the fact that the standard acid added is the *only HCl* present, where in reality there is in addition an indefinite amount of HCl formed in the reaction $Cl_2 + H_2O \rightleftarrows HOCl + HCl$, which would neutralize some of the NaOH formed when NaI and HOCl react. This fallacy has not been pointed out before. It is impossible, therefore, by the use of one sample to determine Cl_2, HOCl, and HCl in the presence of each other. Most of the preliminary experimental work of this paper was concerned with various possible analytical devices, some of which may be briefly described as follows:

(1) DETERMINATION OF TOTAL ACIDITY BY USUAL METHOD—The difficulty in this method lies in the use of indicators in the presence of chlorine and hypochlorous acid.

Methyl orange, rosolic acid, and phenolphthalein were tried out in order to determine which would be best in the titration for total acidity. It was found that neither of the first two would produce any stable color in the presence of Cl_2 and HOCl, no matter how much base or acid was added. It was found that phenolphthalein would give a stable color and definite end-point, provided that at least 1 cc. was used. Furthermore, the end-point depended upon whether this relatively large amount was added drop by drop, or poured in as rapidly as possible, with best results seemingly from the latter method. As an illustration of the lack of exactness of this method, the following data are quoted on the number of cc. of 0.01 *N* NaOH required to neutralize successive 25 cc. portions of the same sample: 17.5, 19, 16.2, 15.5, 16.7. The reactions between the indicator and chlorine and hypochlorous acid led to results, therefore, which were at once nonconcordant and doubtful, unless exactly the same method of titration was used throughout. Attention is directed to the fact that methyl orange cannot under any circumstance be used, though its use is advocated by such an authoritative text as Treadwell.[1]

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[1] Lillie [*Science*, **50** (1919), 259] has shown that there are fortunately some close analogies between many of the properties of metal surfaces and living protoplasm.

[2] *Z. physik. Chem.*, **50** (1904), 465.

[3] *J. prakt. Chem.*, **63** (1901), 141.

[4] *Z. physik. Chem.*, **62** (1908), 199.

[5] *J. Am. Chem. Soc.*, **42** (1920), 896.

(2) REMOVAL OF HYPOCHLOROUS ACID—Methods dependent upon the removal of HOCl were not successful because of the incompleteness of the reactions. For example, a solution was shaken up with pure mercury in order to test the reaction

$$2Hg + 2HOCl \rightleftharpoons HgO.HgCl_2 + H_2O.$$

The oxychloride $HgO.HgCl_2$ first formed is immediately decomposed by the HCl present, and $HgCl_2$ passes into solution, leaving a precipitate of yellow-brown HgO. Subsequent treatment with NaI and titration with $Na_2S_2O_3$ for the determination of chlorine gives highly discordant results. Exposure to strong sunlight in order to decompose HOCl, of course, throws no light upon the relationship between Cl_2 and HOCl since both disappear at a monomolecular rate. The reaction

$$Ag_2O + 2HOCl \rightleftharpoons 2AgCl + O_2$$

and the decomposition in the presence of cobalt nitrate solution, with oxidation of the cobalt to higher valence, were found entirely unsatisfactory as quantitative methods, since both chlorine and hydrochloric acid are also involved.

(3) REMOVAL OF CHLORINE—One of the most promising analytical methods seemed to be found in the removal of chlorine by bubbling air through the solution and collecting the gas in another vessel containing sodium iodide solution, the HOCl remaining behind. de Mallman[2] reports that experiments upon the elimination of chlorine by a current of air showed that free chlorine is totally removed in 5 min. from 50 to 100 cc. solution, and that hypochlorous acid in the small quantities present is little, if at all, affected by aëration. Unfortunately, no data were cited to prove this. These experiments and others to be found do not preclude the possibility, however, of large errors which might arise from difficulties in manipulation, the existence of "free" and "fixed" (possibly hydrated and inactive) chlorine, appreciable decomposition of hypochlorous acid with formation of chlorine, and a minimum concentration below which it is impossible to remove *any* chlorine from chlorine water even in 15 min. As a matter of fact, as will be fully shown, the present researches have met with all of these contingencies and it is therefore impossible to make use of this method alone in determining chlorine and hypochlorous and hydrochloric acids together. It was found possible by careful work to remove the difficulties in manipulation so that, as the following tables will show, it was repeatedly found that the sum of the *two titrations*, after air was bubbled through and the gas collected in a second solution of NaI, checked exactly the total amount of $Na_2S_2O_3$ required by the solution

TABLE 1

		A—Solution Alone (50 Cc.)						B—In Presence of Low-Carbon Steel[1]					
	Expt.	1	2	3	4	5	6	7	8	9	10	11	12
(1) HOCl													
Time Elapsed, Hrs.	(a)	0	24	48	72	96	120	0	24	48	72	96	120
As_2O_3,[2] Cc.	(b)	42.50	41.00	40.00	40.00	40.00	40.00	42.50	18.50	0	0	0	0
HOCl, G. per liter	(c)	0.4460	0.4305	0.4200	0.4200	0.4200	0.4200	0.4460	0.1942	0	0	0	0
HOCl, Moles per liter	(d)	0.0085	0.0082	0.0080	0.0080	0.0080	0.0080	0.0085	0.0037	0	0	0	0
(2) Cl_2 and HCl													
$Na_2S_2O_3$ (Total), Cc.	(e)	47.50	46.50	46.00	46.00	46.00	46.00	47.50	26.50	8.50	2.50	0.00	0.00
$Na_2S_2O_3$(HOCl), Cc.	(f)	42.50	41.50	40.00	40.00	40.00	40.00	42.50	18.50	0.00	0.00	0.00	0.00
$Na_2S_2O_3$(Cl_2), Cc.	(g)	5.0	5.5	6.0	6.0	6.0	6.0	5.0	8.0	8.5	2.5	0.0	0.0
Cl_2, G. per liter	(h)	0.00355	0.003905	0.004260	0.004260	0.004260	0.004260	0.00355	0.00568	0.006035	0.00178	0.00000	0.00000
Cl_2, Equiv. per liter	(i)	0.00010	0.00011	0.00012	0.00012	0.00012	0.00012	0.00010	0.00016	0.00017	0.00005	0.00000	0.00000
NaOH (Back titration), Cc.	(j)	24.00	24.50	23.00	23.00	23.00	23.00	24.00	39.50	55.00	60.00	62.00	62.00
NaOH (from HOCl + NaI), Cc.	(k)	21.25	20.50	20.00	20.00	20.00	20.00	21.25	9.25	0.00	0.00	0.00	0.00
NaOH (Total), Cc.	(l)	45.25	45.00	43.00	43.00	43.00	43.00	45.25	48.75	55.00	60.00	62.00	62.00
HCl (25 Cc. added), Cc.	(m)	20.25	20.00	18.00	18.00	18.00	18.00	20.25	23.75	30.00	35.00	37.00	37.00
HCl, G. per liter	(n)	0.148	0.140	0.126	0.126	0.126	0.126	0.148	0.1734	0.2190	0.2555	0.2701	0.2701
HCl, Moles per liter	(o)	0.004	0.004	0.0035	0.0035	0.0035	0.0035	0.004	0.00475	0.0060	0.0070	0.0074	0.0074
(3) Air Bubbling													
$Na_2S_2O_3$ (1st), Cc.	(p)	35.50	36.00	35.00	36.00	37.00	38.50	35.50	19.00	8.50	2.50	0.00	0.00
$Na_2S_2O_3$ (2nd), Cc.	(q)	12.00	10.50	11.00	10.00	9.00	7.50	12.00	7.00	0.00	0.00	0.00	0.00
$Na_2S_2O_3$ (Total), Cc.	(r)	47.50	46.50	46.00	46.00	46.00	46.00	47.50	26.00	8.50	2.50	0.00	0.00
$Na_2S_2O_3$ (Decomp. of HOCl), Cc.	(s)	7.0	6.0	5.0	4.0	3.0	1.5	7.0	0.0	0.0	0.0	0.0	0.0
Decomp. HOCl, Per cent	(t)	16.5	15.6	12.5	10.0	7.5	3.75	16.5	0.0	0.0	0.0	0.0	0.0
$Na_2S_2O_3$ (Free Cl_2), Cc.	(u)	5.0	5.5	6.0	6.0	6.0	6.0	5.0	7.0	0.0	0.0	0.0	0.0
NaOH (Back titration), Cc.	(v)	24.00	24.50	23.00	23.00	23.00	23.00	24.00	39.50	55.00	60.00	62.00	62.00
Cl_2 (Total), Cc.	(w)	....	....	....	....	....	....	....	7.5	8.5	2.5	0.0	0.0
Cl_2 (Fixed), Cc.	(x)	....	....	....	....	....	....	....	0.5	8.5	2.5	0.0	0.0
Cl_2 (Fixed), G. per liter	(y)	....	....	....	....	....	....	....	0.00177	0.006035	0.00178	0.00000	0.00000
Cl_2 (Fixed), Per cent	(z)	....	....	....	....	....	....	....	6.67	100	100	0.00	0.00

[1] Weight at beginning 57.765 g.; after 120 hrs., 56,9655 g.; loss, 1.4 per cent.

[2] All volumes in this table are on the basis of 0.01 *N*.

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[1] Page 655.

[2] *Compt. rend.*, **168** (1919), 1114.

before air was passed through. These points will be considered in detail in the interpretation of the experimental results, where it is shown that it is impossible to establish any correct relationship between Cl_2 and HOCl, and that such work as de Mallman's is distinctly in error unless properly interpreted.

APPROVED METHOD—The method finally adopted as by far the most accurate depends essentially upon the determination of HOCl by means of arsenious acid, and a combination of this result with Methods 1 and 3, together with the usual method for chlorine and hypochlorous acid in the presence of each other, from which the concentration of all three products may be calculated. The arsenious acid method, depending upon oxidation to arsenic acid by hypochlorous acid, is briefly described in such texts as Treadwell, but no work has been done on the effect upon its accuracy of the simultaneous presence of Cl_2 and HOCl. The actual titration is remarkably simple, definite and rapid, and the results have been found to be capable of repeated reproduction from the same solution, since there is no possibility of secondary reactions with indicators. In order to test out the accuracy of this method for determining HOCl alone and in the presence of the other equilibrium products in the solution, the following experiments were performed.

A solution was carefully shaken for several minutes with freshly precipitated mercuric oxide. The oxide was dissolved by the HCl, but the HOCl, being too weak to react, was left free in the solution, which was then titrated with arsenious acid. In a second test, some of the solution was shaken up with pure calcium carbonate, which reacted only with the hydrochloric acid. This solution was then titrated. It is a singular fact that in both of these cases the results checked exactly with those of a straight titration for HOCl in the presence of both Cl_2 and HCl. The titration must, of course, be carried on very rapidly in order to obtain best results.

EFFECT OF TIME—In following the changes in concentration of Cl_2, HOCl, and HCl with time, in the absence and presence of iron, the following process was adopted. The solution was very carefully made up in order to assure uniform composition and kept in tightly stoppered bottles in the thermostat at 25°. Three portions of 50 cc. each were removed at the same time; one was titrated for HOCl by means of 0.01 *N* arsenious acid solution; the second was acidified with 25 cc. 0.01 *N* HCl, NaI added, and the iodine liberated by both Cl_2 and HOCl was titrated with $Na_2S_2O_3$, after which the excess acid was titrated with 0.01 *N* NaOH, using phenolphthalein as indicators; the third was placed in a Drechsel wash bottle, connected with another similar bottle containing NaI solution, and air bubbled through the original solution for 5 or 10 min. in such a way that the evolved gases would pass through the NaI solution. Both were then titrated with sodium thiosulfate.

In Table I are given the results of the best single series of determinations. Part A shows the results with the solution alone, and Part B in the presence of low-carbon steel. The solutions in both cases were exactly the same, and the three series of titrations on both solutions were made at the same time, once every 24 hrs., using standard solutions which had been repeatedly checked in order to assure accuracy. A great many relationships of rather remarkable nature are at once apparent from an examination of this table, of which only the more important will be specifically pointed out. Part A will first be considered.

As an indication of the accuracy and soundness of the method involved and a justification of the interpretation of results, it is noted that the results in several lines check perfectly; *e. g.*, Line *j* giving the back titration with NaOH corresponds with Line *v* which is the same titration on a different solution after the air-bubbling process to remove chlorine. Lines *g* and *u* for chlorine also agree. Another outstanding relationship is that final equilibrium is reached after 48 hrs., and the amounts of *chlorine*, *hypochlorous acid*, and *hydrochloric acid remain constant* for the duration of the experiment, 120 hrs. There is no reason to doubt the fact that this equilibrium would remain indefinitely in the dark bottle, if conditions were kept constant. This point of equilibrium represents a concentration of 0.008 mole HOCl per liter, 0.00012 equivalents or 0.00006 mole of chlorine per liter; and 0.0035 mole HCl per liter. This gives an equilibrium constant of 0.467 at 25°, considering the concentration of H_2O as constant and the acids completely ionized, which is checked surprisingly well, starting from entirely different concentrations (see Table II). It is a matter of considerable surprise that so relatively great a concentration of HOCl is found, but it is verified by such experiments as titrating before and after exposure of the equilibrium solution to strong sunlight for some time, during which the HOCl is converted to HCl.

TABLE II

A—SOLUTION WITHOUT STEEL

Clear Bottle

				Aëration		
Time Elapsed Hrs.	0.01 *N* As_2O_3 Cc.	0.01 *N* $Na_2S_2O_3$ Cc.	0.01 *N* NaOH Cc.	0.01 *N* $Na_2S_2O_3$ (1) Cc.	0.01 *N* $Na_2S_2O_3$ (2) Cc.	0.01 *N* NaOH Cc.
0.0	42.70	50.00	23.50	41.00	6.40	18.00
24.0	42.60	46.00	17.00	39.20	7.80	18.00
48.0	38.40	41.00	18.00	33.50	7.50	19.00
72.0	36.50	39.00	19.50	34.00	4.00	19.50
96.0	34.50	35.50	20.00	31.00	4.50	21.00
120.0	31.00	30.50	20.00	26.50	3.50	20.50
Dark Bottle						
0.0	46.60	54.00	20.50	40.50	14.00	17.80
24.0	49.00	50.50	16.00	41.50	8.50	17.70
48.0	46.00	47.50	18.00	37.50	10.50	17.70
72.0	43.00	45.50	18.50	38.00	6.40	19.00
96.0	42.00	44.00	19.00	37.00	6.50	17.50
120.0	34.00	42.50	18.50	37.00	4.00	17.50
B—IN PRESENCE OF STEEL						
Clear Bottle						
0.0	30.50	34.50	10.00	35.00	4.00	10.00
24.0	18.00	26.00	18.00	21.00	2.00	18.50
48.0	5.00	14.00	25.50	10.00	1.50	26.50
72.0	0.00	2.50	35.00	2.50	0.00	35.50
96.0	0.00	0.00	35.20	0.00	0.00	35.50
120.0	0.00	0.00	35.20	0.00	0.00	35.50
Dark Bottle						
0.0	30.50	33.50	10.00	31.00	2.50	9.00
24.0	20.00	24.00	15.50	20.50	3.50	15.50
48.0	7.50	12.50	24.00	10.00	2.00	23.50
72.0	0.00	2.50	35.00	2.50	0.00	31.80
96.0	0.00	0.00	35.00	0.00	0.00	32.00
120.0	0.00	0.00	35.00	0.00	0.00	32.00

Another observation which may be made on Part A of Table I is the formation of chlorine by decomposition of HOCl with air. After 48 hrs. this total amount of HCl remains constant (Lines *j* and *v*) and also the concentrations of HOCl and Cl_2 (Lines *d* and *i*, and *e* and *r*), but the amount of chlorine which it is possible to remove by bubbling air through the equilibrium solution becomes gradually less. By comparing Lines *b*, *p*, *q*, *s*, and *t*, it is at once apparent that HOCl, at first decomposing to form chlorine to the extent of 16.5 per cent, gradually becomes more stable towards the action of air as time passes, until after 120 hrs. only 3.75 per cent is decomposed to form chlorine. Just what is the explanation of this anomaly is difficult to say. It may be caused by hydration or polymerization, but most likely is connected intimately with the formation and existence of "fixed" chlorine, which will be presently discussed. This same result has been observed with original solutions of all concentrations, but the more dilute the solution, the more stable it is. It is thus possible to prepare a solution of such concentration that it will be impossible to remove any chlorine by the bubbling of air, either as the free gas or by decomposition of HOCl. Solutions which require a maximum of 22 cc. 0.01 *N* $Na_2S_2O_3$ per 50 cc. in determining both hypochlorous acid and chlorine will not give even from the beginning the slightest trace of chlorine in the second bottle. If the solution is strong enough to require 24 cc., it is possible to remove enough chlorine at once to require a fraction of a cc. of $Na_2S_2O_3$ for titration, but in 24 hrs., though the titer of the original solution is still the same, no chlorine is driven over the series of experiments shown in the table the concentration is over twice the minimum for appearance of chlorine, and it is easy to see why there should be some decomposition of hypochlorous acid. As chlorine is removed, of course the equilibrium is displaced in such a way that HOCl and HCl react to form more chlorine. But *HCl remains constant*, which would, therefore, point to the fact that the greatest factor seems to be the *increasing concentration* of "fixed" chlorine, which cannot be removed from solution by aëration. In reality, therefore, the decomposition of HOCl is apparent only and indeterminate. This is even more clearly shown when iron is present and *all* the HOCl disappears.

Part B of Table I shows the extremely interesting effect of iron upon the equilibrium just discussed. Some time after 24 hrs. all the hypochlorous acid disappears, and after 72 hrs. the chlorine disappears, forming hydrochloric acid, which thereafter remains constant in concentration, showing that finally only one equilibrium is involved:

$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl$$

Lines *j* and *v* again show remarkable agreement. It is to be observed that the ratio of concentrations of HOCl to Cl_2 is at such a value after 24 hrs. that aëration apparently causes complete separation; for Lines *b* and *o*, and *g* and *r* show this. At the next reading, however, HOCl has disappeared, giving no apparent trace with arsenious acid, but 8.5 cc. 0.01 *N* $Na_2S_2O_3$ are still required for the original solution, which can be only chlorine. However, no length of aëration will serve to remove any of this chlorine from solution. This entirely disappears in another 48 hrs., with attendant increase in hydrochloric acid. The Arrhenius theory of active and passive molecules in equilibrium with each other might be very well applied here, but the uncertain catalytic effect of H^+ ions, the formation of hydrogen during reaction with iron, and various possible effects of increasing concentrations of ferrous and ferric salts introduce too many complications. Another plausible explanation of fixed chlorine would be hydrated molecules. The pressure of chlorine gas above a solution is proportional to both the concentration of unhydrated and hydrated molecules, but the proportionality factor is quite different. There is undeniable evidence of the existence of hydrated chlorine in solution. Now, at equilibrium, simply expressed:

$$Cl_2 + H_2O \rightleftharpoons Cl_2.H_2O$$

$$\frac{C_{Cl_2} \times C_{H_2O}}{C_{Cl_2.H_2O}} = K$$

But C_{H_2O} may be considered constant, and hence:

$$\frac{C_{Cl_2}}{C_{Cl_2.H_2O}} = K_1; \text{ or } C_{Cl_2} = K_1C_{Cl_2.H_2O}$$

The distribution ratio of unhydrated molecules gives by Henry's law

$$P = K'C_{Cl_2}$$

(where P is pressure of gaseous chlorine).

Combining with the above:

$$P = K'K_1C_{Cl_2.H_2O} = K_2C_{Cl_2.H_2O}$$

Hence K' and K_2 may be greatly different. Furthermore, the equilibrium is constantly being disturbed because of the existence of another:

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl$$

Under certain conditions of concentration, therefore, a final total effect may be represented by:

$$Cl_2.H_2O \rightleftharpoons HCl + HOCl$$

The gaseous pressure would therefore be regulated to the hydrated molecules, and the fugacity of unhydrated molecules would be negligible. This is merely another way of saying, as de Mallman[1] does, that chlorine is fixed in a quantity proportional to the ratio $Cl_2 : H_2O$, and decreasing with increased ratio and also with increasing acid concentration. If we therefore consider as "free" chlorine only that which *can be* removed by aëration—a sort of excess above the proportionality to the ratio $Cl_2 : H_2O$—de Mallman's generalities agree with these experimental results. The impossibility of removing chlorine gas completely from solution in a short time is verified by the work of Olson,[1] just published, on the equilibrium in chlorine-treated water at 91°. This author says that it may be removed "in a few hours," as contrasted with the 5-min. periods of de Mallman. Olson, however, does not take into consideration any possible influences which might cause the chlorine to disappear in a few hours, such as formation of the acids, without being removed by aëration.

THE CORROSION OF LOW-CARBON STEEL BY CHLORINE-TREATED WATER

Table III discloses several interesting relationships. Low-carbon steel bars of similar composition were

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[1] *Loc. cit.*

TABLE III

Kind of Water and Amount of Chlorine	No.	Diameter In.	Length In.	Surface Sq. In.	Weight before Being Acted on Grams	Weight after Being Acted on Grams	Loss in Weight Grams	Loss in Weight Per cent	Bottle Kept in	Weight Lost per Sq. In.
River + 0 Cl_2	1	0.501	3.031	4.77	76.3380	75.9700	0.3680	0.48	Light	0.0771
River + 2 p. p. m. Cl_2	2	0.501	3.14	4.94	76.6648	76.2920	0.3728	0.47	Dark	0.0754
	3	0.501	3.14	4.94	78.5250	78.1100	0.4150	0.53	Light	0.0840
River + 5 p. p. m. Cl_2	4	0.501	3.14	4.94	78.5926	78.2050	0.3876	0.49	Dark	0.0784
	5	0.501	3.14	4.94	78.7923	78.4000	0.3923	0.50	Light	0.0794
River + 10 p. p. m. Cl_2	6	0.501	3.125	4.91	78.3265	77.9700	0.3565	0.45	Dark	0.0726
	7	0.501	3.14	4.94	78.0265	77.6500	0.3765	0.48	Light	0.0762
Reservoir + 0 Cl_2	8	0.501	3.14	4.94	78.5790	78.2500	0.3290	0.42	Light	0.0666
Reservoir + 2 p. p. m. Cl_2	9	0.339	3.094	3.29	36.7735	36.5230	0.2505	0.68	Dark	0.0764
	10	0.339	3.156	3.36	37.5197	37.2300	0.2897	0.77	Light	0.0862
Reservoir + 5 p. p. m. Cl_2	11	0.339	3.156	3.36	37.4256	37.1500	0.2756	0.74	Dark	0.0820
	12	0.339	3.125	3.33	36.9975	36.6960	0.3015	0.82	Light	0.0905
Reservoir + 10 p. p. m. Cl_2	13	0.339	3.047	3.25	36.4015	36.1260	0.2755	0.76	Dark	0.0878
	14	0.339	3.156	3.36	37.2968	37.0060	0.2908	0.78	Light	0.0865
Distilled + 0 Cl_2	15	0.339	3.125	3.33	37.0810	36.7500	0.3310	0.89	Light	0.0994
Distilled + 2 p. p. m. Cl_2	16	0.339	3.125	3.33	37.1517	36.8100	0.3417	0.92	Dark	0.1026
	17	0.339	3.125	3.33	37.3310	36.9910	0.3400	0.91	Light	0.1021
Distilled + 5 p. p. m. Cl_2	18	0.339	3.156	3.36	38.0679	37.7430	0.3249	0.86	Dark	0.0966
	19	0.339	3.125	3.33	37.2250	36.8830	0.3420	0.92	Light	0.1026
Distilled + 10 p. p. m. Cl_2	20	0.339	3.125	3.33	37.2095	36.9300	0.2795	0.75	Dark	0.0839
	21	0.339	3.156	3.36	37.5665	37.1720	0.3945	1.06	Light	0.1174

placed in solutions of different kinds, and kept in sealed bottles in the light or dark for 100 days. The adhering rust was then carefully removed without abrasion of the unaffected metal, dried at 102°, and reweighed. The loss in weight could then be determined; though more pertinent for purposes of comparison are the results in the weight lost per square inch of original surface. It is at once apparent that greater loss has been sustained in the light than in the dark, due of course to the greater completeness of reactions involving the decomposition of HOCl in light, to form HCl and oxygen. It is also evident that, considering each type of solution separately, rusting or oxidation usually increased with increase in chlorine content, and that corrosion increased in the order: river, reservoir,[1] distilled water.

The least rusting effect is shown by reservoir water containing no chlorine, in the following ratio: reservoir 0.0666, river 0.0771, distilled 0.0994. For the solutions containing chlorine, the least active is river water with 10 p. p. m. chlorine in the dark, and the most active is distilled water with the *same concentration* of chlorine in light. This wide difference is a clear indication of the profound effect of dissolved electrolytes upon the chlorine equilibrium and upon the iron oxidations. Solutions having apparently the same effects are:

2 parts in river water, light, and 10 parts in distilled, dark
0 part in river water, light, and 10 parts in river, light
10 parts in river water, light, and 2 parts in reservoir, dark
2 parts in reservoir water, light, and 10 parts in reservoir, light
2 parts in distilled water, both light and dark, and 5 parts in distilled, light

Because of the extremely great influence of variations of the structure of the steel, rigorous conclusions are not, of course, justified, aside from the general points already considered. After the rust coating was removed at the end of the experiment, the steel bars presented a peculiar spotted appearance, varying from one specimen to another in the ratio of dark area to bright. The corrosion clearly took place on the bright areas, while the dark areas presented very largely the appearance of the original bar with a very tenacious layer of oxide. This differential corrosion in a solution of uniform constitution in which there was uniform contact can be accounted for only by the heat treatment of the original steel, which was probably cold-rolled, so that electrolysis resulted. There was no evidence of any marked pitting due to segregation in the steel structure; hence the effect must be due to heat treatment.

This very delicate test of the uniformity of steel was even more markedly shown by the following experiment. Two highly polished steel bars from the same piece and of the same size were suspended by means of platinum wire in a solution of chlorine in water. One of the bars had been previously rendered passive by immersing in fuming nitric acid, while the other was left active. After 5 min. small bubbles of gas were apparent on the surface of the active bar, and in 15 min. there appeared quite sharply the peculiar mottled condition just described, in which the bright and dark areas were extremely well defined, though the differentiation gradually faded somewhat. The passive bar presented no such phenomenon, though corrosion ultimately set in to much the same extent as with the active bar.

The general average effect of the city water of Nashville upon low-carbon steel containers, such as pipe, is to be found between Nos. 9 and 10 in Table III (reservoir water containing on the average 2 p. p. m. of chlorine), or a corrosive effect of perhaps something over 0.7 per cent loss in 100 days. This supposes that there is to be found no great segregation, which would result in much greater local corrosions, and that outside electrolytes in ground water are not in the action. As a matter of fact, however, the presence of strong local circuits about underground pipes will result in a much greater and much less uniform corrosion than is to be observed in this study made under the most ideal conditions. Flow of water tending to remove adhering rust and presenting new surfaces will also have a large effect. However, in this case of water flowing through a pipe continuously, the electrical conditions are very much more uniform than outside the pipe, and rusting from the inside is always negligible compared with that on the outside, where there may be intermittent exposure to water.

It has been further confirmed that iron subjected to strain or uneven treatment corrodes much more readily than that which has been treated uniformly, the strained part being electropositive to the unstrained. In addition to the differential corrosion due to cold rolling of the bars, there was indication of small grooves parallel to the long axis, due to drawing and resultant minute differences in mechanical strain. Now, in order that rust may be formed, the metal must first go into solution and hydrogen be given off in the presence of oxygen or certain oxidizing agents, thus presuming electrolytic action, as every metallic ion that appears at a certain spot demands the disappearance of a hydrogen ion at another. Iron possesses a specific electrolytic solution tension with regard to a solution of chlorine in water, so that solution results until the osmotic pressure counterbalances the solution pressure. This latter is influenced by segregation, crystal form as related to heat treatment, impurities, temperature, and, of course, the strength of the chlorine solution, and the relative quantities of Cl_2, HOCl, HCl, and, under some conditions as previously shown, hydrated chlorine. It scarcely requires mention that in steel different portions of the same bar, even a very few centimeters apart, possess different solution tensions and behave like different metals if immersed in an ionized solution. In the consequent electrolysis, the ferrous ions liberated at the anodes undergo secondary chemical changes in the presence of such activating agents as chlorides or dissolved oxygen or chlorine itself—the latter two of which act in the very important role of depolarizers—resulting in hydrated ferric oxides, which are formed with a speed of reaction infinitely great in comparison with the other processes.

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[1] Reservoir water is simply the river water treated with alum in settling tanks.

SUMMARY

Rusting occurs in distilled water without chlorine because of the presence of dissolved oxygen, which is of course present in greater quantity than in water containing dissolved electrolytes. In the presence of chlorine, the most active agent is of course HOCl, which, it has been shown, disappears first from the solution. There is no question but that the rust is formed rapidly during the disappearance of HOCl, and then practically stops when the concentration of HCl becomes constant, as shown in Table I. This indicates an equilibrium:

$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl$$

The presence of $FeCl_3$ in solution is of course easily verified.

It has been shown that the reaction

$$H_2O + Cl_2 \rightleftharpoons HOCl + HCl$$

proceeds only very slowly and comes to equilibrium, the constant of which has been roughly determined. It has further been shown that iron has an apparent catalytic action on the reaction, resulting in the disappearance of both chlorine and hypochlorous acid. This has been verified by the very recent work of Olson[1] on the same reaction, carried out at 91° so that $HClO_3$ would be formed. It is pointed out in that work that in order to act as a catalyst the iron must of course exist in two stages of oxidation, and Fe^{++} must reduce ClO^- ion faster than $Cl^=$ does, together with the necessity for a fast enough reduction of Fe^{+++} by Cl^- ion in order to maintain an effective concentration of Fe^{++}. In deciding whether or not the iron has actually acted as a catalyst in materially hastening the final attainment of the equilibrium

$$Cl_2 + H_2O \rightleftharpoons HOCl + HCl,$$

it is at once apparent that, in the presence of chloride, the iron is *almost completely* in the form of the ferric ion, and hence the effective concentration of ferrous ion which can react with ClO^- is negligibly small. The effect is, therefore, practically entirely chemical rather than catalytic in nature, since the equilibrium is entirely destroyed and two of the members disappear.

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[1] *J. Am. Chem. Soc.*, **42** (1920), 896.

ADDRESSES AND CONTRIBUTED ARTICLES

CHEMISTRY'S CONTRIBUTION TO THE LIFE SCIENCES[1]

By A. S. Loevenhart

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THE SERVICE TO BIOLOGY AND MEDICINE OF STUDIES ON OXIDATION

All biological science rests on a tripod of physics, chemistry, and a residual leg of biology which includes all the factors which cannot at present be reduced to the more exact sciences. So intimate is the relation of chemistry to biology and medicine that it is inconceivable that any great advance could be made in chemistry without being reflected in the superimposed structures. I should like to point out the effect on these subjects of two great advances in chemistry. Modern chemistry may be said to have begun with the overthrow of the phlogiston theory of combustion by Lavoisier and the establishment of the mechanism of combustion and oxidation. With this, chemical physiology became a possibility. Oxidation is the only energy-yielding process known to occur to any extent in the body. The hydrolyses and hydrosyntheses which occur in the body are practically isothermic reactions. Lavoisier was not a physiologist, but the relation between oxidation and respiration is so very close that Lavoisier associated with himself the physiologist Sequin, and in their joint article they stated that the bronchi exude a hydrocarbonous fluid and that this is burned in the lungs. They believed that vital oxidation is exactly similar to combustion, that oxidizable material in the body is brought to the lungs and there burned in contact with the oxygen inhaled, the lungs acting as a sort of furnace. Spallanzani first showed that all tissues absorb oxygen and produce carbon dioxide, and through the work of many men it was established that oxygen is absorbed by the blood in passing through the lungs and carried to the tissues where oxidation really occurs. In the effort to determine why such stable substances as proteins, carbohydrates, and fats are burned in the body at a temperature of 37° the group of catalytic agents known as the oxidizing enzymes or oxidases was discovered. The work on the digestive enzymes and the oxidases proved to be the greatest stimulus to the study of the whole subject of catalysis, which has become so immensely important in every phase of chemistry. It is obvious that it was necessary to understand the nature of combustion before vital oxidation could be attacked. The recent work on slow oxidation and the peroxide theory of oxidation of Traube, Baeyer, Engler, and many others emphasize the differences between vital oxidation and combustion.

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[1] Presented at the General Session of the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

A. S. Loevenhart

There are many phases to the subject of vital oxidation, which may be divided as follows:

(1) The mechanism by which oxidation is brought about in living matter, including the subject of the oxidizing enzymes.

(2) The nature of substances capable of being oxidized by living matter. Thus it is known that certain substances which are readily oxidized outside the body, such as carbon monoxide and oxalic acid, escape oxidation in the living organisms.

(3) The relation of chemical constitution to oxidizability in the body. Thus it is known that, whereas *d*-glucose and *d*-fructose are readily oxidized in the body, *l*-glucose and *l*-fructose escape oxidation entirely. Apart from the stereochemical relation, constitution is often the determining factor in oxidizability.

(4) The relation of oxidation to the energy requirements of the organism.

(5) The relation of oxidation to other chemical processes occurring in the organism. Thus when oxidation is interfered with, abnormal products of metabolism may result.

(6) The effect of various substances and conditions on vital oxidation.

(7) The relation of oxidation to vital activity, by which is meant the relation of oxidation to stimulation and depression, including the symptoms and morphological changes produced in the tissues as a result of alteration in oxidation.

(8) The question whether any substance other than molecular oxygen can furnish the body with physiologically available oxygen.

ORGANIC PEROXIDES IN MEDICINE

It is obviously impossible to discuss these various phases of oxidation in the time at our disposal, and I desire only to indicate the great scope and interest connected with this subject. I should, however, like to say that the analogy of the organic peroxides and of the oxidases, first pointed out by Kastle and Loevenhart,[1] is interesting from a chemical point of view. Furthermore, the group of organic peroxides and other organic oxidizing agents are interesting and important from another standpoint. During the war the most important and useful antiseptic substances proved to be those whose antiseptic activity is attributable to their oxidizing properties—the hypochlorites and the chloramines. The antiseptic action of these substances is not interfered with by the presence of protein, to which is attributable their great merit as antiseptics for wounds. Furthermore, it has been shown by Hektoen[1] that certain oxidizing substances greatly increase the formation of certain bodies of an antitoxin-like character. This would lead us to believe that oxidation plays an important role in the process of immunity to disease. Amberg[2] has shown that certain organic oxidizing substances markedly reduce the local inflammatory reaction to such irritants as mustard oil, and Arkin[3] has likewise shown that they stimulate phagocytosis.

It may be that we shall here find an antiseptic which can be administered intravenously in bacterial blood infections. It is probable that these substances will prove valuable not so much in consequence of their antiseptic action, but rather by the stimulation of natural immunological processes, that is, the production of antitoxins, and bacteriolysins, and the stimulation of phagocytosis. You are, of course, aware that we have no drug at the present time which is useful in general bacterial infections. In all those cases in which we have specific substances which are useful in general infections, such as syphilis, relapsing fever, and malaria, the infectious agent is a protozoan and not a bacterium. Such a substance would be a boon to mankind.

Both from the standpoint of the development of important antiseptics and substances useful in the treatment of infection, and also from the standpoint of the elucidation of biological oxidation, I believe the organic peroxides to be a most important group requiring further work on the part of the pure chemist. We should know more of the possible methods of preparing these substances, and a much larger number should be prepared than are at present known. We need to investigate many such substances in order to arrive at one having exactly the right properties. Thus if the substance be too active an oxidizing agent, it will be toxic and, on intravenous injection, it may alter the blood pigment, or it may be used up in oxidizing substances in the blood so that it will not reach the tissues. Furthermore, the substance should be soluble in water, and, as a wound antiseptic, it would be a great advantage if it were soluble in glycerol. I am inclined to believe that those substances whose oxidizing action is due to the presence of oxygen would prove to be more valuable than those substances whose oxidizing action is due to the presence of chlorine.

Let us pass on to another chemical achievement and observe its effect upon pharmacology and medicine. The treatment of disease by drugs reaches back into remotest antiquity. The earliest documents extant tell of the uses of drugs and poisons. Various views have been expressed regarding the origin of the belief in the efficacy of drugs in the treatment of disease. From the vile and revolting character of many remedies which have been used, it has been suggested that it had its origin in the belief that diseases are sent by a Deity, and that revolting things were used as a sacrifice to appease the wrath of the Deity. Against this view is the oft-repeated observation that carnivorous animals at times instinctively consume certain plants. Then again, many remedies are used by primitive peoples which are in no sense offensive. It may be that the view held sway that since the Lord created all things, including diseases, and sent them to punish man, He must have placed in the world a cure for all diseases and left it to the ingenuity of man to find the remedy. At any rate, when illness plagues a man, he and his family are so constituted that they will search for a remedy as long as life lasts, and in the course of human history it is hardly possible to find an accessible substance which has not been used in the treatment of almost every disease. They proved all things but it was impossible to hold fast only to that which was good. Their observations were crude and faulty. Every case was treated and no one knew what the course of the untreated disease would be, and yet by this method great advances were made in the course of the ages. Thus, opium was introduced into medicine before the Christian era, and cinchona bark in the treatment of malaria, and mercury in the treatment of syphilis were introduced by the same method at a much later period, but their introduction antedated scientific medicine or chemistry.

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[1] *Am. Chem. J.*, **26** (1901), 539; *Therap. Monatsh.*, **19** (1905), 426.

[1] *Trans. Chicago Pathol. Soc.*, **8** (1911).

[2] *Z. Exp. Med.*, **2** (1913), 19; *J. Pharmacol.*, **10** (1917), 209.

[3] *J. Infect. Dis.*, **11** (1912), 427.

THE DEVELOPMENT OF CHEMOTHERAPY

The second great chemical achievement whose effect on pharmacology and medicine I desire to discuss briefly was the isolation of the alkaloids of the plants in the first half of the last century. With this achievement, medicine took a great step forward and it is difficult to realize its service in the field of medicine. This work made it possible to assay some of the important crude drugs chemically, the pure principles could be employed when indicated, dosage became more accurate, and it prepared the way to hypodermic medication. Following the isolation of the alkaloids, their composition was determined and, with the rise of organic chemistry, the problem of their constitution presented itself. Although all these substances are complicated, great advances have been made in the study of their constitution, and in some instances it has been completely solved. When the chemist had determined the constitution of these substances, pharmacologists began to inquire into the cause of their remarkable biological properties and sought to determine the groups within the molecule responsible for them This led to the production of other closely related substances, and some of these artificial substances have proved to be more useful than those occurring in nature. This work naturally developed into the general proposition of determining the relation of chemical constitution to pharmacological action. This subject came into greatest prominence with the investigations of Ehrlich and his co-workers, who introduced the term chemotherapy to signify this field of work. Ehrlich started out with the proposition that arsenilic acid is useful in the treatment of spirillar infections, including the diseases caused by the trypanosomes and the *treponema palladum*, the latter being the infectious agent in syphilis. Starting out with arsenilic acid, they proceeded to vary the compound in every conceivable way and to determine what particular grouping possessed the greatest therapeutic power against these infections. The 606th substance studied proved to be arsphenamine (salvarsan), the most valuable drug that has been produced in the treatment of syphilis. This substance had the disadvantage of being difficultly soluble in water, so that its administration presented considerable difficulty. In order to determine how the substance might be rendered soluble without destroying its therapeutic value, the work was continued, and after about 350 more substances were prepared they struck upon neoarsphenamine (neosalvarsan). This is by no means, however, the last word in the treatment of syphilis. The beautiful work of Jacobs and Heidelberger on the chemical side, and of Brown and Pearce on the biological side, at the Rockefeller Institute, will surely result in the introduction of certain compounds which will be of great value in the treatment of certain types of syphilis. The interest to us in all this work is, first, that it is of the greatest possible practical importance to humanity and, second, that it requires the most complete coöperation between organic chemists, pharmacologists, and physicians. To my mind, it is today the most promising field in any of these subjects. The difficulty presented is in getting full coöperation between these groups of workers. This difficulty, although great, must be overcome. It will require large appropriations, as appropriations go, for scientific work, and the men engaged in it must be willing to pool their interests and have full confidence in one another. I think we scientific men are too often thought of as being of the prima donna type, each one insisting that he shall be the whole show. I am sure that this is a calumny and that in the search of valuable new drugs, groups can easily be formed of men who will be willing to pool their interests and each one receive simply his share of credit for the success in the work. Those of us who were engaged in the research work of the Chemical Warfare Service must certainly have been impressed with the effective work done by the chemists and pharmacologists working in close coöperation. It is a remarkable fact that we actually know more about the pharmacological effects of certain groups of substances, which were worked on only for a brief period of one year and which were designed for the destruction of human life, than we know about the most important substances which have been used in the treatment of human disease for a period of 2000 years. Men working in time of war with the exaltation of patriotism were willing to coöperate; the exaltation of relieving human suffering should certainly be no less, and we must look forward to the formation of many groups of workers in this field if we are to fulfil our obligation to society.

CHEMICAL TRAINING FOR THE MEDICAL RESEARCH WORKER

Perhaps I may be permitted to say a word in conclusion regarding the importance of chemical training for those who are going into medicine, and especially those who are going into the research side of medicine and the medical sciences. Every research man in medicine should receive a most thorough training in one of the fundamental sciences upon which his work rests. It may be either chemistry or physics; it cannot be both, because each of these subjects is too great for a man really to become expert in both. It has been my experience that a man cannot become a real chemist, develop the best chemical technique, and, above all, the chemical point of view and mode of thought, after going into biology. It would seem that a chemical training cannot often be superimposed upon biological training, but must precede it just as the foundation must precede the construction of a building. The reason for this is not clear to me, but it may be that the biological work when once entered upon seriously is so enthralling that it is impossible for one to go back and so deeply immerse himself in chemistry as to absorb its spirit. A man can hardly develop into a high type of chemist simply as a means to an end; for the time being it must be studied for its own sake. It amounts virtually to this, that more chemists must go into medicine and the medical sciences. The man must first become a chemist or a physicist, and later a physician. With the mere rudiments of chemistry which the average medical student receives we must be satisfied for the present, because the medical curriculum is very full, but for those who are going to advance medicine from the experimental side in the future, we should advise that they be professional chemists or physicists first.

THE SUGAR INDUSTRY OF FRANCE SINCE THE WAR[1]

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As Chief of the Sugar Division, Engineering Section, of the War Damage Board, American Commission to Negotiate Peace, the author was assigned the task of estimating the damage done by the war to the sugar industry of France. M. Saillard, chief chemist of the Association of Sugar Manufacturers of France, was consulted in his splendid laboratory. M. Veuville, the president of the association, furnished a letter of introduction which proved very useful. M. Barbarre, designer and builder of sugar factories, M. Gilbert, manager of the largest beet-sugar factory in France, and M. Alexander, editor of the *Journal of the Sugar Manufacturers*, gave helpful advice and furnished invaluable data and statistics.

The continental blockade, in 1806, prevented the entry of colonial cane sugars into Europe, and the occasion was seized by Delessert and Mathieu de Dombasle to perfect the experiments of Achard, and the first French sugar factory was installed. Napoleon recognized the value to the nation of the new industry and granted subsidies and complete exemption from taxation. Later, the blockade was raised and Europe was flooded with cane sugar, and it was not until the Restoration and the Second Empire that the beet-sugar industry triumphed; but from that time on it made rapid and certain progress.

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[1] Presented at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

[2] Formerly Major, Chemical Warfare Service, A. E. F.

Sugar Factory of Montescourt-Lizerolles—Department Aisne, Arrondissement de St. Quentin

The extent to which the French sugar industry had grown before the war is shown by the fact that 7 per cent of the capital invested in industry in the invaded regions of Northern France was placed in the sugar industry. The extent of the damage suffered is shown by the fact that, out of 217 sugar factories in France in 1913, over 142 were damaged, and, for the most part, completely destroyed. Measured on the basis of production in tons, 66 per cent of the sugar industry of France was wiped out.

There were in operation in 1913, 213 sugar factories; and in 1917, only 65. In 1913 there were produced 877,656 metric tons of refined sugar, and in 1917 only 185,000 tons. In 1913 the balance of the sugar trade showed 78,739 tons of surplus sugar exported; and in 1917, 397,746 tons imported, with a decrease in consumption from 703,126 tons to 563,479 tons. The sugar shortage of France is about 716,132 tons per year since the loss of her factories.

The 142 sugar factories which were in the war area were damaged, on the average, to the extent of being 85 per cent destroyed; and to rebuild them or replace them at present prices of machinery and building materials, would cost about $89,000,000. The land remains and building materials exist, but the grounds and buildings represent only about one-half of the value of the average beet-sugar factory. The machinery and mechanical appliances represent the other half, or a value of $45,000,000, but their replacement from other parts of France is impossible for the present. The great steel mills, foundries, engine works, and factories where sugar machinery and equipment were made, were, for the most part, located in the same region, notably around St. Quentin, Lille, and Douai, and these great industrial plants suffered the same fate as the sugar factories.

It is hoped that it will not be out of place to repeat here a portion of a report written by the author while still in France, which was quoted by Major Charles P. Wood, in the March issue of *Sugar*.

During the 1914 advance of the German armies, very little damage was done to the sugar industry, but, on the other hand, due to the scarcity of metals and materials in Germany in 1917 and 1918, every factory which was behind the 1918 line of maximum advance was absolutely stripped of all copper, brass, bronze, belting, rubber, and electrical equipment. The copper coils, brass plates, and bronze tubes of pans, evaporator effects, juice heaters, etc., were removed; sometimes by unbolting the bottom of the pan or effect, and letting it fall to the floor below, and then removing tubes, coils, etc., through the bottom; and often by tearing away the insulation, and cutting a large section out of the side of the pan or effect by means of an oxy-acetylene flame, and removing the copper and bronze from the interior through this hole. The sugar boiler's brass proof sticks, the brass stuffing boxes, the brass frames of peep glasses of pans, evaporator effects, etc., the copper-lined spouts and troughs of juice filter presses, all centrifugal screens and back screens, all brass and bronze bearings on engines, pulley shafts, etc., were removed by unbolting or breaking off. All electric generators, alternators, motors, distribution boards, etc., were removed, a loss which, in various cases, amounted to 16, 25, 50, and as high as 65 motors for one factory.

The French factories were, in general, good and compared quite favorably with the general run of American factories. Machines were well made, well installed, and conservatively operated. In France, a sugar factory works about 90 to 110 per cent of its rated capacity. The beet-sugar factories of our largest American firm handle, year in and year out, about 170 per cent of their rated capacity. Consequently, it can be seen that to produce a given quantity of sugar requires more machinery and equipment in France than in America. There exists a contrast between French and American methods in the matter of *raperies* or juice annexes. These annexes have boilers, cutters, and a diffusion battery, and pump the diffusion juice through a small pipe line to the central factory. In America very few juice annexes exist, probably only the one in Idaho; but in France they are quite general. The 142 factories destroyed in Northern France had 70 juice annexes which suffered the same fate. One factory, a 3,000-ton mill near Cambrai, had 14 juice annexes situated around the central factory, at distances varying from 1 to 15 miles.

Another contrast exists in the matter of product. While practically all the American sugar factories and refineries, including even the smallest beet-sugar factories in the West, produce white granulated sugar, the general run of French factories produced white crystals, or No. 3 sugar, which was shipped to a refinery. The refineries put out very little granulated sugar, their product being in the form of domino sugar or cubes. The largest refinery in France puts all of its 1,500 tons per day through the "Adant" system, of which the product is 85 per cent domino, and the remaining 15 per cent powder and small broken lumps, incidental to the manufacture of domino. The coast refineries which handle the raw cane sugar from Africa and the French colonies make principally the *pain de sucre* or sugar loaf, a hard conical lump of refined sugar, weighing 2

Sugar Factory of Tricot—Department Oise, Arrondissement de Clermont—between 1914 and 1918 Lines According to Maps, Destroyed in Battles of June 1918 kilograms. This product is demanded principally by the colonial trade.

The French manufacturers and refiners make and sell whatever their trade demands; which, so far, has been principally the sugar loaf and domino; and it is quite likely that when bans are lifted, so that they can buy machinery and equipment outside, they will proceed to reëstablish along the same general lines that existed before the war. Reconstruction presents enormous difficulties, and will doubtless entail long delays, but sooner or later the French factories will be rebuilt.

At the present time reconstruction in France is making enormous strides.

Of the 7,000,000 acres of arable land laid waste by the war already over half has been again put under cultivation. 2163 kilometers of railroad, together with bridges, tunnels and locomotives were completely destroyed, and to-day circulation has been restored over the whole; out of 600 bridges destroyed, 475 have been rebuilt; out of 370 passenger stations destroyed, 200 have been rebuilt; out of 11,500 factories destroyed, 3500 have been rebuilt and 3500 are now under construction. In 1919 France had to import 150,000,000 bushels of wheat, and in 1920 she is having to import only 30,000,000.

This is really wonderful progress in reconstruction, but the sugar industry, because of its requirements in specially constructed machinery and mechanical appliances, because of the enormous amounts of copper, brass, and electrical equipment required, has not been able to do so well. A communication from Monsieur Le Hay, president of the Association of Sugar Manufacturers of France, dated July 5, 1920, states that only 60 French sugar factories are now in working order.

The accompanying photographs, taken by the writer while on field trips for the War Damage Board, in January and February of 1919, will show clearly the average condition of 142 sugar factories after the war.

SCIENTIFIC SOCIETIES

PROPOSED NEW DEPARTURES IN GOVERNMENT CHEMICAL WORK

Dr. F. G. Cottrell, director of the Bureau of Mines, and Dr. C. L. Alsberg, chief of the Bureau of Chemistry of the U. S. Department of Agriculture, faced an audience that was quite generally out of sympathy with the proposed plan to provide government machinery for developing inventions of scientific workers in the various laboratories of the Government, on Friday evening, October 15, 1920, at the Chemists' Club of New York. They had been invited to present their views on this subject before a joint meeting of the American Institute of Chemical Engineers, the American Section of the Society of Chemical Industry, the New York Section of the American Chemical Society, and the New York Section of the American Electrochemical Society. The meeting was largely attended by representatives of the chemical and allied industries, many of whom had come prepared to discuss the subject and express their views in opposition to the proposed plan.

Dr. David Wesson, president of the American Institute of Chemical Engineers, who presided, opened the meeting with the reading of an introductory paper, in which he recommended the consolidation of the various scientific departments and bureaus of the Government. He deprecated the fact that government scientists are poorly paid, but did not favor permitting them to work out inventions from which they would benefit personally, on the Government's time.

Dr. Alsberg was then called upon to present his views on the issue, and he asserted that much misunderstanding of the proposed measure had resulted from incorrect newspaper accounts of what was the true intent of the legislation desired. As far as the Bureau of Chemistry of the Department of Agriculture was concerned, the whole object was to provide some means of developing inventions made by laboratory workers during the course of their regular routine or research work, so that these inventions would not be lost to the public. Dr. Alsberg stated emphatically that his chemists were not engaged in the business of inventing, but, as is the case with every laboratory staff that is efficient, they could not help developing new ideas and processes in the course of their investigational work. In order that such "by-product inventions," which might often prove of great value to industry, should not be lost to the public, it was proposed to create machinery for developing them and incidentally to provide some reward to the inventor. In his Bureau Dr. Alsberg had organized the office of development to take charge of such work, not with the view of competing with any industry, but rather to bring the matter to that stage which would insure for it a proper reception on the part of the industry.

Dr. Alsberg characterized Dr. Wesson's plan of consolidating government scientific work as "inefficient, ineffective and impossible." He pointed out that Congress appropriates money only for the solution of specific problems and not for the advancement of the sum total of human knowledge of the various sciences. Hence all government laboratory work must be of a practical nature and must be performed by experts in each particular field. It would be illogical, for instance, Dr. Alsberg maintained, to have work on mining problems, paper and pulp, fertilizers, and therapeutic serums all referred to a central laboratory and expect expert treatment of it. Coördination is needed, but not fusion, said Dr. Alsberg. He further remarked that it is a mistake to compare the Government to a corporation. It can be compared only to a holding corporation which exercises supervision over the policy of a large group of corporations. Turning again to the subject of developing inventions of government laboratory workers, he stated that his turnover of chemists in the past year had amounted to nearly 40 per cent, due largely to the fact that the salaries paid are not adequate and that no adequate inducement is offered to hold good men in the service. He dwelt on the fact that very often chemists of the Bureau while coöperating with certain industries see glaring examples of waste and inefficiency for which they are able to provide a remedy by marshaling information they have acquired in the course of their experimental work. Some practical method should be found whereby such developments may be passed along for the benefit of all. He cited the discovery of the effectiveness of calcium arsenate in combating the boll weevil as an example of governmental invention, and stated that all methods of preparing this compound had been patented by the Government in order that no one should be obliged to pay tribute to a private concern or individual for using these patents, as had been the case with lead arsenate.

In conclusion Dr. Alsberg stated that the proposed plan of developing inventions of government employees was the result of considerable thought given to the subject by government officials, who were confronted with conditions and not with theories, and who were endeavoring to solve the problem in a manner calculated to redound to the greatest good of their employers, the American public.

Dr. Cottrell was then asked by the chairman to present his views on this important subject, and after discussing the object of granting patents in general and laying emphasis on the fact that patents are granted to promote progress in science and useful arts rather than to reward inventors, he took up the bill before Congress in detail. He stated that the feeling existing in some quarters, that there had been an attempt on the part of those interested in the bill to push it through without giving its provisions proper publicity, was not founded on fact. He related the efforts which had been made to secure publicity for the measure in trade journals and elsewhere without success.

The measure under discussion passed the Senate on March 22, 1920, as Senate bill 3223, and was introduced in the House of Representatives, where it was referred to the Committee on Patents. This committee having before it a bill known as the Nolan bill, which provides for reorganization of the Patent Office, decided to tack the provisions of Senate bill 3223 onto the Nolan bill or H. R. 11984, making it Section 10 of that bill. This bill was passed and then sent to the Senate. During all this time, little or no comment on the matter of promoting government inventions had been aroused, but as soon as the amended Nolan bill with the invention provisions reached the Senate, a number of amendments were suggested, and Congress adjourned before final action was taken on the bill, although the Senate on June 4 passed certain amendments to Section 10. The matter in italics in the following text was eliminated by the Senate amendment while the matter in capitals was added. Therefore, by ignoring italicized portions and reading the capitalized portion as part of the bill the reader has the wording of the bill as it will go to the Conference in December 1920.

SECTION 10. That the Federal Trade Commission be, and hereby is, authorized and empowered to accept assignment of, *or license or other rights or powers under, to develop, to issue or refuse to issue licenses under, to encourage the industrial use and application of, and otherwise to administer,* on behalf of the United States under such regulations and in such manner as the President shall prescribe, inventions, patents and patent rights which said commission deems it to the advantage of the public to be so accepted, as these may from time to time be tendered it by employees of the various departments or other establishments of the Government, *or by other individuals or agencies;* and to coöperate, as necessity may arise, with scientific or other agencies of the Government in the discharge of the duties herein set out, and the Federal Trade Commission is hereby authorized and empowered to LICENSE AND collect fees and royalties for licensing said inventions, patents and patent rights in such amounts and in such manner as the President shall direct, and shall deposit the same with the Treasurer of the United States; and of the total amount of such fees and royalties so deposited a certain percentum, to be determined by the President, shall be reserved, set aside, and appropriated as a special fund to be disbursed as directed by the President to remunerate inventors for such of their inventions, patents and patent rights contemplated by this section as may prove meritorious and of public benefit; PROVIDED, THAT NOTHING HEREIN SHALL BE CONSTRUED TO GIVE SAID COMMISSION OR ANY OTHER GOVERNMENTAL AGENCY ANY AUTHORITY TO ENGAGE IN THE MANUFACTURE OF ANY SUCH INVENTION OR PATENTED ARTICLE.

The Commissioner of Patents is hereby directed to grant all patents and record all assignments and licenses contemplated by this section without the payment of any fee.

Dr. Cottrell said a great deal of the opposition to the measure that has developed seems to hinge on the fact that the Federal Trade Commission has been designated to handle these inventions. He did not feel that lack of confidence on the part of some in the Federal Trade Commission should be considered sufficient cause to abandon the plan. If the Federal Trade Commission has not fulfilled all that was expected of it, said Dr. Cottrell, steps may be taken to reorganize it, but it is wrong to attempt classifying the work under any other head than this Commission.

He compared the present situation to the condition that has confronted universities and colleges where pure scientific research work carried on in the laboratories often leads to discoveries of commercial value. To develop these the Research Corporation was organized several years ago, and it has been functioning with success. Congress, however, objects to turning over government problems to quasi-public bodies, preferring to tie up all government development work with a regularly constituted governmental agency. It became necessary, therefore, in connection with this legislation, either to create a new organization to handle the patents or to rely on an existing agency such as the Federal Trade Commission which, according to Dr. Cottrell, is the logical agency in this case.

There is nothing mandatory in the bill, declared Dr. Cottrell. Its provisions should be carefully studied, and it is particularly important to establish a fair basis of remuneration for the inventor. Pooling the returns in one fund to be shared equally under specified conditions by the inventors seems to be fairer in Dr. Cottrell's opinion than to reward the inventor with a return based on the financial yield from his specific invention. In conclusion he denied the allegation that the Government intends to compete with private industries and is seeking the passage of the bill before Congress to this end.

The discussion was opened by R. P. Perry who asserted that the passage of the legislation under discussion and carrying out its provisions to their logical conclusion would help the chemical industries of the rest of the world at the expense of those of our own country. He bitterly denounced any attempt on the part of the Government to place itself in competition with private enterprise. He also felt that the proposed legislation would give government employees an unfair advantage over other scientists in the matter of securing patents. In Mr. Perry's opinion the proposed legislation is not desired either by chemists, the industries, or the people. Messrs. H. A. Huston, Sperry, and Weston were strong in their convictions that the Government should keep hands off patent development, and should continue to give service through its various bureaus rather than attempt to establish any form of patent control or license system.

Dr. H. E. Howe suggested that constructive criticism and suggestions be offered by those assembled so that a satisfactory solution to the problem might be arrived at. No further comments of a constructive nature were forthcoming, however. The meeting closed with short statements by both Dr. Cottrell and Dr. Alsberg in which they reiterated their position with regard to the proposed legislation and asked the representatives of industry to study the matter thoroughly and give constructive suggestions for meeting the condition which confronts the directors of our government laboratories in taking care of the inventions of their laboratory workers.

GRASSELLI MEDAL AWARD

At the joint meeting of the American Section of the Society of Chemical Industry with the New York Section of the Société de Chimie Industrielle, held in Rumford Hall, Chemists' Club, New York City, on Friday evening, October 8, 1920, the first Grasselli medal was awarded to Dr. Allen Rogers, for his paper entitled "Industrial Uses for the Shark and Porpoise."[1]

The medal was established in 1919 by the Grasselli Chemical Company of Cleveland, Ohio, to be awarded annually for the paper presented before this Section of the Society of Chemical Industry which should, in the opinion of the Medal Committee, offer the most useful suggestions in applied chemistry. The presentation was made by Dr. Marston Taylor Bogert.

Dr. Rogers was born in Hampden, Maine, May 22, 1876, and graduated from the University of Maine in 1897 with the degree of B.S. in the chemistry course. For three years he remained at his Alma Mater as instructor in chemistry, receiving the M.S. degree in 1900. He continued his graduate work at the University of Pennsylvania and was awarded the Harrison Fellowship for 1901–2. In the latter year, the University conferred upon him its Ph.D. for a research concerned with certain complex inorganic acids, the results of which were published in the *Journal of the American Chemical Society*.

For two years longer he remained at the University, first as Senior Fellow, lecturing to graduate students on analytical and physical chemistry, and later as instructor in organic chemistry.

In June 1904 he entered the employ of the Oakes Manufacturing Co., Long Island City, N. Y., as research chemist, where his investigations on problems related to the leather industry led to several patents being taken out by the company.

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[1] *J. Soc. Chem. Ind.*, **39** (1920), 9*t*.

In September 1905 he returned to the ranks of the teachers, as professor in charge of industrial chemistry at Pratt Institute, Brooklyn, N. Y., the position he still occupies. Taking up his duties with characteristic energy and enthusiasm, he organized a course in industrial chemical engineering, making use of miniature plants to train young men for positions as foremen and superintendents in large-scale manufacturing establishments. This undertaking has been conspicuously successful from the outset, and already many of the graduates hold prominent places of great responsibility in our chemical industry.

Gardiner and Son

Allen Rogers

Dr. Rogers is the author of the "Manual of Industrial Chemistry," in the preparation of which he was aided by over forty distinguished collaborators. This standard treatise has gone through three editions, and is now used as a text in more than fifty colleges and technical schools. He is also the author of "Elements of Industrial Chemistry" and "Laboratory Guide of Industrial Chemistry" (2 editions).

After this brief biographical account Professor Bogert said in part:

> For many years Dr. Rogers has made a special study of leathers and tanning, until he is now widely recognized as one of our foremost experts in this important field. Patents have been granted him for various processes of treating leather, and other patents are pending. His most interesting work in this direction is that recorded in the paper for which the medal is awarded, namely, the utilization of the shark and porpoise as sources of leather. In making the award, the Medal Committee entered upon their minutes a note expressing their judgment that Dr. Rogers' paper was a record of work accomplished by him in recovering oils, and manufacturing fertilizers and fine leathers, through which he contributed much information and some entirely new processes in applied chemistry.
>
> In the time of our country's need, he promptly and patriotically sacrificed all personal selfish interests and volunteered for military duty, being commissioned Major in the Chemical Warfare Service, where he was put in charge of the Industrial Relations Branch, a post of considerable responsibility, involving indirectly classification of industries into more and less essential, and determining recommendations of exemption from military duty for those chemists who were more needed at the factories than at the front. Many a plant would have had to close its doors, or seriously curtail its output, and the military preparation of the country would have been considerably delayed, but for the energy and ability with which Major Rogers fulfilled his duties. When the war had been won, he was equally active in aiding chemists discharged from the Army to get back into lucrative positions once more, an assistance which was deeply appreciated by many demobilized colleagues.

ABSTRACT FROM SPEECH OF ACCEPTANCE

By Allen Rogers

The commercial utilization of the shark is a matter that has interested me for several years and if I have done anything to interest others in my friends of the deep, it is, of course, very gratifying. Sharks have always been considered as scavengers, and of no benefit to man. My work, however, has shown me that they have some good points in their favor, and if we take advantage of them I feel confident that a great industry may eventually be established. Already much has been accomplished in this direction. A fairly large plant is in operation at Morehead City, N. C., where the fish are caught, the skins removed, the livers rendered for oil, and the flesh converted into fertilizer stock. Another plant is located at Sanibal Island, Fla.; and at the tannery in Newark, N. J., about one thousand skins are being treated each week. Plans are now under way for establishing other stations at various points along the Atlantic and Pacific Coasts, while the existing plants will be greatly enlarged.

CLEVELAND MEETING OF THE AMERICAN ELECTROCHEMICAL SOCIETY

The thirty-eighth meeting of the Society, its first in Cleveland, was held on September 30, and October 1 and 2, 1920. The attendance was smaller than expected, undoubtedly due to the greatly increased cost of travel. Those who came, some 175 visitors, were rewarded by fine papers and snappy discussions, interesting visits to laboratories and plants, and unexcelled social events and intercourse.

The Local Committee, under the direction of Dr. N. K. Chaney, of the National Carbon Co., aided by L. C. Drefahl, A. R. Bullock, and Mrs. E. R. Grasselli as heads of sub-committees, arranged visits to many of Cleveland's industrial plants, an afternoon at the Nela Park laboratories, and engaging diversions for the visiting ladies.

Among the papers read and discussed were the following: M. R. Wolfe and V. de Wysocki studied and measured the heat losses through the electrodes and their water-cooled rings, on a 6-ton Heroult steel furnace making steel castings, finding 123 kw. lost out of 650 kw. on the furnace, or 18.7 per cent of the power taken by the furnace. A. M. Kuhlman and A. D. Spillman measured the heat carried out of the same furnace by the steel and slag, making the heat content 476 to 520 cal. per kg. of slag, and 303 to 325 cal. per kg. of steel. M. L. Hartmann, A. P. Sullivan, and D. E. Allen, of the research laboratory of the Carborundum Co., reported measurements of the electrical resistivity of nine commercially used refractory materials, at temperatures which were slowly raised from cold to 1500° C. All showed great reduction, from nearly nonconductors when cold to below 10,000 ohms resistivity (per cm. cube) at 1500°; the actual values when 1500° was reached were

	Ohms per Cm. Cube
Bonded Carborundum (Carbofrax C)	8590
Silica Brick	8420
Magnesia Brick (Burned Magnesite)	2500
Bauxite Brick	1100
Fireclay Brick, Grade A	890
Bonded Carborundum (Carbofrax B)	745
Zirconia Brick (Natural Mineral)	412
Chrome Brick	41
Recrystallized Carborundum (Refrax)	1.6

The tremendous variations, of the order of 5000 to 1, point to interesting applications of this information to electric furnace work. It was pointed out in the discussion, however, that these resistivities are considerably changed by keeping the materials several hours at 1500°, sometimes being reduced 75 per cent, and that the final values obtained as constants on long heating are the quantities greatly desired.

F. A. J. Fitzgerald and G. C. Moyer noted the deterioration of nickel resistors in electric furnaces due to the absorption of sulfur. J. Kelleher spoke of curious flaring of the arcs observed in electric furnaces, making the observations through a pinhole diaphragm. Oscillograph records were also taken, while automatic current regulators were employed. The "arc" is found to consist normally of a set of small arcs around the periphery of the electrode; when the electrode approaches too near the slag, a large arc also appears, which is broken as the regulators raise the electrode, leaving only the small arcs working on a small portion of the electrode. This cuts down the current, and the regulators begin to lower the electrode. When the electrode almost reaches the slag, the small arcs suddenly spread over the whole end of the electrode, the current is largely increased, and the cycle of events described is repeated.

E. S. Bardwell described electric smelting of manganese ores at Great Falls, Montana, with a balance sheet of the heat distribution in the furnace which showed some 72 per cent of the electric energy usefully applied. The losses in the slags were large, one slag having nearly 20 per cent of manganese. It was pointed out in the discussion that the manganese losses in the slags varied in all cases inversely as the sum of Al_2O_3, CaO, and MgO, so that they were directly controllable by controlling the slag composition.

J. W. Richards described the first American installation of the Söderberg continuous self-baking electrode. This consists of three 32-in. round electrodes, used three-phase, in a 2000 kw. ferromanganese furnace at the plant of the Southern Manganese Corporation at Anniston, Alabama. These have worked continuously during July and August, the stoppages in 28 days in August on account of the electrodes being only 13 min.; carbon electrode consumption 14 lbs. per 1000 kw.-hrs. In the discussion it was stated that a 37-in. electrode of this design is now working in South Africa, and that the Stavanger Steel Company in Norway is successfully using Söderberg electrodes on a 6-ton tilting Heroult furnace.

E. A. Keeler described the advantages of exact conductivity measurements upon solutions as a means of recording and controlling industrial processes. For example, a test weight of a sugar sample is added to a given volume of a salt solution of known conductivity, and the per cent of sugar is determined from the decreased conductivity of the solution. If the sugar is already in solution, a fixed weight of salt is added to a fixed volume of the solution, and the conductivity measured.

C. J. Rodman and T. Spooner described a new, portable laboratory standard cell, in which a compact, concentric form is substituted for the familiar H type. Tungsten wire leads are used, and some particular methods of purifying the cadmium and its salts devised. Constancy to within 0.0001 volt in over two years is attained.

J. W. Richards called into question the direct relationship of electric current to electrochemical action at the cathode. At the anode the anion is of invariable valency, and a constant relation seems to subsist between the electrical current and the amount of anion liberated. It is to be noted that present electrical theory postulates negative electrons passing to the anode as the fundamental conception of the flow of electric current. At the cathode, varying amounts of the cation may be liberated, according to its varying valency, and the question is therefore asked, whether the amount of cation liberated is not determined *chemically*, as that amount which was united with the quantity of anion liberated, rather than fundamentally or primarily by an electrical relation. In the absence of definite proof of the existence of positive electrons, or, let us say, in the presence of a unitary theory of electrical current flow, the question is not without justification.

The session of Saturday morning was largely concerned with electroplating and metal refining. A. L. Ferguson and E. G. Sturdevant described investigations of the deposition of brass from cyanide solutions, accompanied by careful measurements of the potential and the effects of various additions. F. C. Mathers and W. H. Bell described negative results in the use of addition agents in plating tin from alkaline solutions. E. F. Kern described the electrolytic refining of tin, getting best results with stannous sulfate baths acidulated with 7 per cent H_2SO_4, and with the addition of peptone or gelatin. F. C. Mathers showed that gums, resins, or oleic acid are satisfactory addition agents to prevent the crystallization of lead depositing from alkaline electrolytes.

F. W. Skirrow and E. R. Stein described the production of hydrogen peroxide by electrolyzing potassium acid sulfate solutions with platinum anodes, crystallizing out the potassium persulfate formed, and distilling the crystals with sulfuric acid and water. A good yield of hydrogen peroxide is thus obtained.

E. A. Richardson and L. T. Richardson showed as the result of long-duration, air corrosion tests that the presence of copper reduces the corrodibility of pure iron and, to a greater extent, that of steel. In the case of steel, they suspect the manganese present to enhance the effect of the copper; this conclusion was called in question in the discussion, it being maintained that manganese had the opposite effect. The authors also stated that chromium had a still greater effect in reinforcing the protective action of copper. This conclusion was not disputed, since stainless steels prove the strong protective action of chromium.

W. D. Richardson of Chicago, in a paper of 34 pages, discussed the details of the solution of metals in acids as related to their corrodibility. In view of the use of accelerated tests to determine the resistance of metals to atmospheric corrosion, these tests are of importance. The principal point brought out was the great importance of various catalytic bodies, which are often present, in facilitating or retarding solution in acids. The influence of other factors, such as that of hydrogen, oxygen, carbon dioxide, halogens, and cathodic action, were also investigated.

All the papers had been printed in advance and distributed to members of the Society before the meeting. As a consequence discussions were lively and intelligent, and contributed discussion from a distance was frequently submitted. This has proved to be a highly successful method of bringing about a high-class scientific meeting.

A referendum of the Society as to making the metric system the exclusive legal system of weights and measures of the United States showed 483 in favor to 107 against. A majority of the members present did not favor increasing the annual dues by $1.50 in order that the Society might join the Federated American Engineering Societies. J. W. RICHARDS

LEHIGH UNIVERSITY
SOUTH BETHLEHEM, PA.
October 11, 1920

CALENDAR OF MEETINGS

American Petroleum Institute—Annual Meeting, Washington, D. C., November 17, 18, and 19, 1920.

American Institute of Chemical Engineers—Winter Meeting, St. Charles Hotel, New Orleans, La., December 6 to 9, 1920.

American Association for the Advancement of Science—Annual Meeting, Chicago, Ill., December 27, 1920, to January 1, 1921.

American Ceramic Society—Annual Meeting, Deschler Hotel, Columbus, Ohio, February 21 to 26, 1921.

American Chemical Society—Sixty-first Meeting, Rochester, N. Y., April 26 to 29, 1921.

NOTES AND CORRESPONDENCE

REPORT OF E. S. CHAPIN, PARIS REPRESENTATIVE OF THE TEXTILE ALLIANCE, INC., TO THE DYE ADVISORY COMMITTEE OF THE STATE DEPARTMENT, SEPTEMBER 29, 1920

I will divide the report into four parts: first, the Herty Option colors; second, the Reparation colors from the impounded stocks; third, German daily production and the future; and fourth, general comments.

HERTY OPTION

The orders placed with the Cartel by the Textile Alliance from assignments to them of licenses under the first six months' allocation amounted to 1,700,000 lbs. Up to September 7 the Cartel had delivered or were preparing to ship 1,200,000 lbs., approximately 70 per cent of the total orders. Of this, 374,000 lbs. have been shipped from Reparation sources; and 800,000 lbs., or 400 tons, have been shipped under the Herty Option. There have been 124,000 lbs. of cancellations, about 7 per cent of the total orders, leaving 397,000 lbs., that is, about 23 per cent, still to be delivered.

Orders placed were divided into vats and non-vats; 460,000 lbs. of vats and 1,240,000 lbs. of non-vats. The vat color orders are of especial interest. Of these 83 per cent have been delivered. The cancellations of vat colors were practically negligible, *i. e.*, only 3,000 lbs., or about two-thirds of 1 per cent. Of the 385,000 lbs. of vat colors delivered, 134,000 lbs. have come from Reparation and 251,000 lbs. have been shipped under the Herty Option.

The most notable aspect of the delivery of colors under the Herty Option is the change in the attitude of the Germans from apparent hostility to active coöperation with the Textile Alliance. In February and early March they had offered against this option the small sum of 192,000 lbs., and gave little promise or encouragement of being able speedily to deliver further quantities. In the last four or five months, however, they have been able to deliver an additional 600,000 lbs.

As regards the vat colors, in March they stated that they could deliver about 40,000 lbs. and held out no promise or encouragement of being able to ship large quantities in the future, but since then they have shipped 210,000 lbs.

The record of the Badische Company is especially interesting in connection with this change of attitude and improvement in performance by the Germans. This company received 43 per cent of the orders placed, that is, 732,000 out of 1,700,000 lbs.; and of the vat colors, 70 per cent of the orders, that is, 318,000 out of 460,000 lbs. To date, the Badische have delivered 625,000 lbs., that is, 85 per cent of their total orders, and of the vat colors they have delivered 280,000 lbs., or 89 per cent.

For months in letters and personal interviews various representatives of the Cartel have insisted upon the *bonne volonte* of the Cartel and their desire to do everything possible to coöperate with the Textile Alliance and to send their colors to the consumers in America.

Some comparisons are at times interesting and to the point. I was told by a British authority that Great Britain had secured on the free market up to August first, 200 tons of German dyes. This should be compared with our figure of 400 tons as of September 7, plus the unknown quantity imported into the United States under license through other channels. It is quite evident that the Cartel has made unusual efforts to send a large proportion of their free production to the United States. That they are anxious to sell to the United States came out quite strongly during my last trip to Germany. The representative of one of the factories asked me if they could not secure some more Herty Option orders. I was in Frankfort on September 1 when the Cartel was holding a special meeting, and had at that time several interviews with representatives of different factories in which they showed the greatest desire to coöperate in numerous ways to place their colors in America.

REPARATION COLORS FROM THE IMPOUNDED STOCKS

In the first place we must note that the impounded stocks were not so large in tonnage as was currently believed last fall. Erroneous information then placed the impounded stocks at 40,000 tons, of which one-half was to be divided among the Allies. As a matter of fact, the total of the August 15 inventory of impounded stocks was 20,000 tons, of which 50 per cent was to be distributed among the Allies. There were in the impounded stocks 13,000 different types of colors. The distribution of the impounded stocks among the Allies was made in two divisions: first, a division of 5200 tons, commonly known as the "5200 Ton" Agreement or the Protocol of November 4. According to this arrangement the different Allies were permitted to select certain colors not to exceed a certain percentage of each color and a certain gross tonnage; that is to say, the United States was allowed to choose 10.22 per cent of any color in the impounded stocks, not to exceed a gross tonnage of 1500 tons. France, for instance, was allowed to select 15 per cent of any color, not to exceed a thousand tons, etc. Great Britain had the same allocation as the United States.

The United States allocation of 1500 tons was taken in two different lots, known, respectively, as the 300-ton lot and the 1200-ton lot. The 300-ton lot included the 374,000 lbs., above mentioned as having been shipped against the first six months' allocation orders. It also included 76 tons of indigo 20 per cent paste, which were given by the United States representatives in Paris last winter to Belgium. The balance of the 1500 tons has been called the 1200-ton lot.

The cause of the division of the 1500 tons into two lots ordered at different periods was the method of providing payment. The Textile Alliance received, as is well known, the money for the 374,000 lbs. of reparation dyes applied against the first six months' allocation orders before placing orders with the Cartel; but for the balance of the 1500-ton lot had neither orders nor money. Further sound policy required that money must be in hand, or underwriting guarantees of payment, before the dyes should be ordered. In this emergency, in the interest of the United States and of American consumers, a few individuals, with the support of your Underwriting Committee, came forward and by providing underwriting saved the balance due the United States from the 5200-ton agreement.

The balance of the stocks was divided among the Allies according to a different system. The dyes were divided into 13 groups according to their nature, that is to say, whether Alizarin Red, vat color, indigo paste, direct cotton, or acid, and so on. These different classes were divided among the Allies according to different percentages, roughly corresponding to the needs for home consumption of the Allies. Thus the percentage of the United States for indigo paste was 5 per cent, because this product was not needed in the United States, whereas for Indanthrene Blue GCD, which was needed, the percentage was 55 per cent.

The second division, known as the Pool, that is to say, the balance of the impounded stocks, amounted roughly to 5000 tons. Here again we were confronted with the financial difficulty of the necessity of providing funds or underwriting before we could place orders for our allocated portion of dyes from the Pool; again the difficulty was solved by the underwriting already mentioned. The Pool contained many types in very small amounts and also many types and mixtures that it was not desirable to order. The gross of our orders after the New York office and the Paris office of the Textile Alliance had scanned the figures of the Pool amounted to approximately 500 tons.

To summarize, the total of our orders from the impounded Reparation stocks amounts to 2000 gross tons, or, to be exact, 4,435,635 lbs.

Of these 2000 tons, 190 tons have been applied to fill orders under the first six months' allocation, approximately another

100 tons of importable colors have been sold to consumers in the United States; 76 tons of indigo paste were given by our representatives in Paris last winter to Belgium, and 450 tons of indigo paste have been sold to China. The balance is about 1200 tons.

The Textile Alliance has rented a warehouse in Antwerp in which these 1200 tons are now stored or to which they are in process of shipment. Of the 1200 tons in the warehouse about one-half can be classed as colors that may be imported into the United States. We have thus approximately 600 tons of nonimportable colors.

Early realizing that the amount of nonimportable colors from the impounded stocks would be considerable, on my first trip to Germany in May I took up with the Frankfort people the matter of exchanging nonimportable colors for importable colors. At that time the answer was that they had nothing to give in exchange. On my last trip, however, I found a different state of affairs. The manufacture of the factories had increased considerably during the summer and there was a willingness to make trades. I have also taken up with our various Allies the matter of exchanging our nonimportable colors for importable colors and this is still in process of negotiation.

By securing all of the colors from the impounded stocks that were of value and to which the United States had the right, we have thus built up a reserve of products which can be used either directly for the benefit of the consumers of the United States or else indirectly by exchanging the nonimportables for the importables. After making all the exchanges possible of nonimportable for importable colors we are preparing to sell the balance of nonimportable colors.

I have already compared the 400 tons of dyes the United States has received under the Herty Option with the 200 tons received by Great Britain from the free market. In this matter of the shipment of Reparation dyes a brief statement of what our Allies have been doing will be interesting. The British found considerable difficulty in distributing the Reparation dyes allocated to them. Dr. Philippi, of the Cassella Color Company, made a trip to England in August in order to assist in facilitating the distribution and avoiding further delay. Last April, Herr von Weinberg and his secretary, Director Molner, made a trip to Italy, in the course of which they assisted the Italians similarly in distributing their dyes and avoiding the difficulties found in dealing with such a complicated matter. The French government distributed colors very actively among French consumers but nevertheless there was considerable complaint. Belgium's problems were simpler because of the small amount of colors received and they appear to have been dealt with quite successfully. None of the above-mentioned countries have had to contend with the most serious problems which faced the United States, namely, the Rotterdam strike and the distance from Germany.

GERMAN DAILY PRODUCTION AND THE FUTURE

The treaty provides that the Allies may exercise an option on 25 per cent of the daily production of the German factories for the period specified in the treaty. It further provides that in the event that this production is below the normal the Allies may require 25 per cent of the normal production.

The question of just what "normal production" means has not yet been settled by the Reparation Commission. In the meanwhile the commission has exercised this option and is accepting 25 per cent of the actual production of the German factories. This daily production it has been arranged to divide among the Allies very much in accordance with the scheme by which the Pool was divided among the Allies; that is to say, the different colors produced are divided into classes according to their nature, and divided among the Allies according to percentages corresponding approximately to the estimated needs of the various Allies.

During last winter the various Allies exercised very stringent supervision over the activities of the German factories. In order to break this control the Germans came forward in January and offered to supply all the needs of the Allies irrespective of the treaty stipulations, provided control was lifted from the factories. This proposition was accepted and in February and March the different Allies were busy in preparing a list of the requirements to be submitted to the Germans.

Our representatives were not in accord with the proposal, but as the French, Belgian, and Italian governments were insistent on their needs of dyestuffs and that the proposal should be accepted, our representatives did not feel that they could negative an offer on the part of the Germans to supply to the Allies all their requirements. Accordingly in May, after much discussion and many meetings, the lists of the requirements of the different Allies were forwarded to the Germans. This proved unacceptable to the Germans and this first proposal accordingly fell to the ground. Since then a new protocol has been drafted by the Dyestuff Bureau of the Reparation Commission. This new arrangement has not yet been discussed with the Germans and indeed has not yet been put into final shape by the Bureau. It is expected that the new protocol will be discussed by the various bodies of the Reparation Commission in late October and will be ready for discussion with the Germans in November.

In the meanwhile the Germans are putting aside 25 per cent of their daily production and this is allocated to the Allies in accordance with class and percentage. In order that the Allies may know what the Germans are making, on the fifteenth of each month the Germans submit a statement of the 25 per cent due the Allies from their production of the previous month. This includes every color produced, a statement of 25 per cent of the amount produced, and the price to the Allies, which according to the arrangement is the lowest price quoted during the month of production to any buyer, German or otherwise. A brief analysis of the quantitative and qualitative production of the German factories for the past six months will be of interest.

The total production of the German factories in the month of February, the first month for which a daily production list was submitted, was 1600 tons, approximately 10 per cent of their pre-war capacity. This production has steadily increased; 2400 tons in March, 3300 tons in April, 3800 tons in May, 4800 tons in June, and 5500 tons in July, or from approximately 10 per cent of their pre-war capacity in the course of six months to $33^{1}/_{3}$ per cent.

GENERAL COMMENTS

From the standpoint of the consumers of dyestuffs in the United States, this rapidly increasing production on the part of the German factories is not so satisfactory as might at first appear, for a large part of the increase in production is not the Herty Option colors, the colors desired by the consumers in the United States, but the big bulk colors, the colors that are being made by American manufacturers.

Take the three months—May, June, and July. The total production by all the German factories of vat colors and fast alizarin colors, which are especially desired by consumers in the United States, was approximately 800 tons. During the same period the production of indigo 20 per cent paste, direct cotton colors, acid colors, and sulfur colors amounted to 8800 tons, that is to say, eleven times as much as the production of vat colors and fast alizarin colors.

Further, while the production of the vat and alizarin type dye is increasing slowly from 228 tons in May to 261 tons in June and 272 tons in July, the production of the type of dyes made in the United States is increasing by leaps and bounds, from 2400 tons in May to 2800 tons in June and 3800 tons in July. This large German production of dyes of the same type as are being made in the United States is evidence of the necessity of special protection for the American industry. The relatively small German production of dyes of the Herty Option type explains the 23 per cent of the first six months' allocation orders still to be delivered.

The question naturally arises whether the Germans cannot produce more of the special colors desired by the United States. The arrangement which is being considered by the Reparation Commission aims to effect this purpose. The Germans do not like the necessity of putting aside 25 per cent of every color which they make during the month for the Allies and especially dislike the necessity of holding this 25 per cent against future orders, more or less problematical. Accordingly the Germans are inclined to consider a permanent proposition which will do away with the necessity of their putting aside 25 per cent of their daily production. The future of the supply of German colors to the United States is linked up with this permanent proposal. According to all indications when I left Europe, it seemed almost certain that the permanent proposal would be adopted in the course of a few months.

ALLIED CHEMICAL AND DYE CORPORATION

The merger of the General Chemical, Barrett, National Aniline & Chemical, Solvay Process, and Semet-Solvay Companies has been approved by the boards of directors of the companies concerned and the question of ratification is now before the stockholders.

The formal announcement by the stockholders' committee stated:

> * * * * * that the boards of directors of the respective companies have approved the plan of consolidation of the General Chemical Company, the Solvay Process Company, the Semet-Solvay Company, The Barrett Company, and the National Aniline & Chemical Company, Inc. Copies of the plan and deposit agreement will be mailed to stockholders as promptly as practicable.
>
> The name of the new corporation will be the Allied Chemical and Dye Corporation.
>
> The authorized capital stock will not exceed $65,000,000 7 per cent cumulative preferred stock, shares $100 par value, and 3,000,000 shares of common stock without par value.
>
> It is estimated that the outstanding capitalization of the new company, based on the deposit of all outstanding stock of the consolidating companies and after elimination of intercompany holdings, will be: Bonded indebtedness of consolidating companies undisturbed $9,493,000; 7 per cent cumulative preferred stock, $39,374,300; common stock without nominal or par value, 2,119,677 shares.
>
> If current earnings should be substantially maintained, as the committee believes they will be, and if substantially half of such earnings in excess of preferred dividend requirements should be distributed in regular quarterly cash dividends on the common stock of the new company, as the committee would favor, holders of such common stock may expect to receive regular quarterly cash dividends thereon at the rate of $6 per share per annum.
>
> The committee of stockholders of the consolidating companies in charge of the consolidation will be composed of the following gentlemen, who have been designated for that purpose by the boards of the respective companies:
>
> William H. Nichols, chairman of the board of the General Chemical Company
> W. H. Nichols, Jr., president of the board of the General Chemical Company
> E. L. Pierce, president of the Solvay Process Company
> R. W. Swift, treasurer of the Solvay Process Company
> H. H. S. Handy, president of the Semet-Solvay Company
> A. W. Hudson, vice president of Semet-Solvay Company
> Eversley Childs, chairman of the board of The Barrett Company
> W. Hamlin Childs, president of The Barrett Company
> Orlando F. Weber, chairman of the board and president of National Aniline & Chemical Company, Inc.
> Wm. J. Matheson, director National Aniline & Chemical Company, Inc.

Dr. Wm. H. Nichols is chairman of the committee, and Clinton S. Lutkins, 25 Broad Street, is the secretary.

The Guaranty Trust Company will be the depositary for all classes of securities and will issue transferable deposit certificates against deposits of stock under the plan. The Bankers Trust Company will act as the registrar of deposit certificates.

"CRIPPLING A GREAT WORK"

The Kny-Scheerer Corporation
of America
New York

Oct. 6th, 1920.
In your reply refer to: N. E. F.

Journal of Industrial & Engineering Chemistry,
Room 343, No. 1 Madison Ave.,
New York City.

Gentlemen:

Our attention has just been called to an editorial appearing in your September number, under the heading, "Crippling a Great Work."

The reputation of your Publication prevents the thought that this article was written by you in a spirit of malice. No doubt the author who prompted the article, and whose patriotism has been heralded through the trade as "———'s Patriotism Pays," took advantage of your good nature and had the article written and published by you. An article of this kind can only be written and published with a view of injury to the party in question; so far as the general public is concerned, they are not interested.

The Kny-Scheerer Corporation of America is owned and controlled solely by born Americans; men who lent their services in many ways to their Government during the recent great struggle, and who did not measure their patriotism by the dollar-mark.

We feel that you believe in a square deal, and think that you will agree with us that in the article above referred to, we have not been treated fairly or squarely; and that your reputation for fair play will prompt you to extend to us the same courtesy that you would want extended to yourselves under similar circumstances.

This letter is written without feeling or resentment on our part as against your Publication, and we trust that you will receive it in the same spirit.

Yours very truly,
The Kny-Scheerer Corporation of America
(Signed) N. E. Franklin
President

FRANKLIN FILTER PAPER

To the Editor of
"The Journal of Industrial and Engineering Chemistry"
N. Y. City.

My Dear Dr. Herty:

Permit me to correct some erroneous statements published on page 955 of the Journal in reference to the "Franklin Filter Papers" which caused so much unpleasantness at the recent Chemical Exposition.

First of all, this line of filterpapers, manufactured by Messrs. Macherey, Nagel & Co., Dueren, who are represented in this country by myself, had been broadly advertised as German manufacture for at least 6 months previous to the exposition, and I feel certain that nobody ever intended to sell this paper under false pretense. Chemically treated paper for accurate gravimetric analysis is not being manufactured in this country, and the only other paper of this kind shown at the exposition was made in France and in England. Therefore, we have all reasons to believe that the parties who happened to be under the entirely mistaken impression that the German papers shown were offered as American manufacture were not American manufacturers of such material—as these do not exist—, but we are sure that those parties started the trouble either for pure business reasons or for reasons of personal dislike against the exhibitor of the material. My careful investigation of the entire incident leads me to believe that the latter alone was the basis of the attack. It is very unfortunate indeed, that a young business-man can be influenced by personal feelings to such an extent as to willfully misrepresent the facts to the management of the exposition. Naturally, these people were not aware of the fact that the paper had been advertised broadcast as German manufacture. The entire unpleasant incident is so much more difficult to explain as the same young business man has been selling the identical line of filterpapers for years under the name of "Dr. Nagel's" filterpaper; evidently be promoted Mr. Nagel to the Ph.D., in order to sell larger quantities of the paper made by the firm of which Mr. Nagel happened to be sales manager, while Mr. Macherey was in charge of the technical end of manufacturing operations, having held the position of Chief Chemist of Schleicher & Schuell for many years.

This willful shifting of the brand of the filterpaper by the same party which was so upset about the present label under which the paper is being marketed brings me to the second part of my argument. The present label of this line of filterpapers, showing Benjamin Franklin's picture, has been designed by a most patriotic American who served as Lieutenant in the Chemical Warfare Service during the war and whose ancestors have been patriotic Americans for many more generations as [*sic*] those of the man who started the entire unpleasantness. The reason for the change of label was only the difficult pronounciation of the manufacturers name: Macherey, Nagel & Co. No other reason was in the mind of the man who conceived and carried out the idea of the Franklin label, and each advertisement and circular on this material published by my firm showed plainly that the material was manufactured in Germany.

As mentioned before, neither the management of the exposition nor the editorial staff of the Journal was aware of these facts, but were willfully misled by a man who evidently let his personal feelings run away with his brains.

Yours very truly
(Signed) Herman A. Holz,
President,
Holz & Company, Inc.

P. O. Box 152,
Madison Square Station,
New York, N. Y.
October 14th, 1920

PLATINUM THEFT

President D. R. Anderson, of Randolph-Macon Woman's College, Lynchburg, Va., reports that its supply of platinum, amounting to 682.579 g., has recently been stolen.

WASHINGTON LETTER

By J. B. McDonnell, Union Trust Building, Washington, D. C.

INDUSTRIAL ALCOHOL

Establishment of an Industrial Alcohol and Chemical Division of the prohibition unit of the Bureau of Internal Revenue, effective October 15, has been announced.

Work heretofore assigned to the Division of Technology will be subdivided and administered by the Industrial Alcohol and Chemical Division and a new division to be known as the Permit Division, and the title of Division of Technology will be discontinued. Dr. A. B. Adams, former head of the Division of Technology, has been appointed head of the Permit Division, and J. M. Doran, assistant head of the old Division of Technology, has been made head of the Industrial Alcohol and Chemical Division. The Bureau's announcement stated that

> The change is made necessary by the increase in the work devolving upon the Division of Technology. The Permit Division will examine and pass upon applications for the manufacture of alcoholic products; determine all nonbeverage uses of intoxicating liquors and limitations of such uses; fix standards for manufactured articles containing alcohol; examine bonds; conduct trade investigations to determine whether products are bona fide and whether permitted articles are manufactured in accordance with approved formulas. The Industrial Alcohol and Chemical Division will have supervision of the construction and operation of industrial alcohol and denaturing plants, and control of the work of the plant officers; develop uses of denatured alcohol by laboratory work and research; examine denatured alcohol samples; examine samples of toilet articles, flavoring extracts, etc., and report the result of analysis to the Permit Division.

Establishment of a separate division in the prohibition unit of the Internal Revenue Bureau was urged upon officials some months ago by a large number of manufacturers and users of industrial alcohol at a conference held here. The situation in which the industry found itself at that time, because of the ofttime ridiculously hampering restrictions placed upon it by the prohibition forces, was made clear. Action on the request of the producers and consumers was necessarily delayed because of the illness of Commissioner of Internal Revenue Williams. While for the most part the executive officials in charge of the work of the Bureau recognized the justice of the complaint of the industry and the real need for relief, it is understood that action probably would have been taken sooner but for the attitude of some of those directly in charge of the affected divisions of the prohibition unit. However, action finally has been taken apparently along the right lines, and there should result an end to the petty hamperings of a vital industry by executive officials in their enforcing of the purely prohibition sections of the law.

THE DYE CENSUS

Comparison of 1914 imports, and production in the United States of dyes by classes in 1917, 1918, and 1919, will be contained in the forthcoming census of dyes and coal-tar chemicals of the United States Tariff Commission and will make available for the first time valuable comparative information.

The table was prepared by A. R. Willis, and other members of the chemical staff of the Commission who have been at work on the census, for the purpose of placing dye statistics in a form that can be readily interpreted by the consumer. It has not yet been worked out to absolutely final figures, because of inability to get all reports affecting totals. Certain preliminary figures, however, are tabulated below.

Type of Dye	Per cent of Total Imports	Per cent of Total Production		
	1914	1917	1918	1919
Acid dyes	20.21	.....	.....	18
Basic dyes	6.53	.....	.....	7
Color lakes and spirit-soluble dyes	3.29	2.03	.....	3
Direct dyes	22.34	24.32	21.01	23
Mordant dyes	9.69	9.06	9.32	8
Sulfur dyes	15.35	33.91	40.53	27
Vat dyes (including indigo)	22.53	0.63	5.61	15

It should be pointed out, in the case of the vat dyes, that synthetic indigo formed a very large part of the total classed as vat dyes in the table in 1919. While synthetic indigo also was included in the 1914 import figures, this dye formed a larger proportion of the total vat dyes produced here in 1919 than in the 1914 imports.

Varying conditions and developments in the history of our dye needs and manufacturing ability, of course, affected the production of these various classes of dyestuffs. In general, these fluctuations were accounted for in the preliminary statement of the census made by Dr. Grinnell Jones, chief chemist of the Commission, in his address last month at the Exposition of Chemical Industries in New York City.[1]

Statistics now being gathered for publication will give considerably more details regarding our dye industry than have heretofore been available. The War Trade Board has begun compilation of statistics showing the total licenses granted for dye imports during the fiscal year ending with June last. While the licenses granted by the Board will not mean in all cases actual imports, they will give as accurate a statement of the needs and desires of American dye consumers as it is possible to obtain in the opinion of War Trade Board officials.

Preliminary figures show that licenses were granted, during the fiscal year ending with June last, for dye imports from Germany amounting to 3,500,000 lbs., while licenses granted for imports from non-enemy countries totaled approximately 8,000,000 lbs., the largest proportion of which came from Switzerland, imports of more than 5,000,000 lbs. being licensed by the Board from that country.

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[1] This Journal, **12** (1920), 959.

While these War Trade Board statistics would be valuable in themselves, their value will be further enhanced by the publication by the United States Tariff Commission of a census of dye imports during the same fiscal year, using the Norton 1914 import census as the basis. An interesting comparison will be afforded by these two censuses of imports. Such import statistics as are regularly collected and made public by the Government through the Bureau of Foreign and Domestic Commerce of the Department of Commerce do not approach the detail desired, and such statistics as the Commission proposes to publish are not elsewhere available.

While the Tariff Commission is being discussed it might be interesting to note that Commissioner Culbertson in a speech recently delivered before the Southern Tariff Congress at New Orleans declared that the development of the American dye industry "reads like a fairy tale" of achievement.

Dyes, of course, are far from entitled to occupy the center of the chemical stage at all times, but to an ordinary layman it is somewhat surprising to find that the Government is conducting experiments with dyes as a possible cure for tuberculosis, under the direction of Dr. McCoy of the Hygienic Laboratory. Dr. McCoy is working in coöperation with Dr. Paul Lewis, of the Phipps Institute, Philadelphia, who also is engaged in conducting experiments along this line.

FEDERAL TRADE COMMISSION COMPLAINTS

Recent complaints issued by the Federal Trade Commission include charges of bribery of employees by the United States Color & Chemical Co., Inc., Boston, Mass., and the Seymour Chemical Company and Alexander S. Mann, Providence, R. I., textile finishing materials.

NAVAL RESEARCH LABORATORY

Bids for the construction of a Naval Research Laboratory to be established at Bellvue, D. C., were opened recently by the Navy Department. Bids will be opened later for supplying of laboratory equipment which will be desired. The laboratory is for the purpose of testing and experimentation on ordnance and ordnance materials and supplies and other articles, and other naval uses calling for laboratory research. The laboratory is to be established out of an appropriation of $1,500,000 given by Congress in 1917. Because of the wording of the appropriation, some of this fund has been used for other purposes, so that there is now available about $1,000,000 for construction of the plant.

THE DYE BILL

While little or nothing is being done in Washington at present —for obvious reasons—by supporters of the dye bill, the bill retains the same parliamentary status at the coming session of Congress in December as when that body adjourned last session. There is no doubt but that strong efforts will be made to have definite action taken by the Senate at this session. It should be borne in mind, however, that, in case of failure of the measure to get final action by Congress, both Senate and House, before adjournment of next session, it will lose all advantage it now has as a bill already passed by the House, and will have to go over the same steps which it began so many months ago.

October 16, 1920

PARIS LETTER

By Charles Lormand, 4 Avenue de l'Observatoire, Paris, France

Signs of scientific and industrial activity are beginning to reappear. The annual industrial exposition held at Lyons (the Lyons fair) has just opened. This covers a district important in the chemical industry.

Owing to its proximity to the Alps and the Cevennes, the region of Lyons is particularly fortunate in possessing numerous waterfalls. The chemical works accomplished a great deal during the war, and since that time have adapted their manufactures to new needs. The pyrite mines of Saint-Bel, which are in this district, produce annually 270,000 tons, thus providing also for the development of all the industries dependent on sulfuric acid.

Exhibits at the Lyons fair by the different firms of the region include notably fats, stearin, glycerol, and gelatin. One company alone produces monthly 150 tons of oleic acid, 30 tons of glycerol, and 1,000 tons of soap.

Also to be noted are tanning extracts and natural coloring matters, 100,000 tons of which are annually produced in the region.

All the large industries of the district which use illuminating gas are recovering the benzene from the gas, in order to provide raw materials for the manufacture of dyes. Considerable effort has been made along this line.

The production of dyes during the past year was 1391 tons in the Lyons district alone, while in 1913 all the French industries together produced only 1000 tons.

Mention should also be made of the exhibit of photographic and pharmaceutical products by the well-known scientists, MM. Auguste and Louis Lumière, and also of the active efforts in the manufacture of textiles and artificial silk.

Professor Grignard now occupies the chair of organic chemistry of the Faculty of Sciences at Lyons, and he is actively engaged in promoting the necessary liaison between science and industry.

NICKEL PLATING OF ALUMINIUM

The French Society of Civil Engineers has just held its opening meeting of the season. An interesting paper was presented by M. Léon Guillet, professor at the Conservatoire des Arts et Métiers, who discussed the problem of the nickel platiug of aluminium. This is not a new question, but all the patents dealing with this subject have not given satisfactory results.

The problem is that of developing the use of aluminium for coatings and obtaining a metal which is not attacked by different liquids, particularly sea water.

Good results are not obtained with perfectly polished aluminium. Neither should there be a too pronounced scouring. M. Guillet has obtained excellent results by a cleaning with jets of sand under light pressure (600 g.), followed by a nickel plating of 0.06 mm., then a copper plating of 0.012 mm., and finally a second nickel plating of 0.06 mm., the nickel and copper plating being effected in baths by the ordinary procedure.

Pieces thus prepared have been perfectly successful. Tests of stamping, of folding, and of burnishing, as well as the action of caustic soda, have proved the good quality of the nickel plating obtained.

The process has not been patented, and M. Guillet is quite ready to give further explanation to those interested. His sole interest is only to facilitate and popularize the use of aluminium.

SUGAR

M. Paul Kestner has recently installed in Saint-Gaudens (Haute-Garonne) and in Belgium, in the region of the Sambre, two large factories for the sugar fields. In the factories he is preparing "whole" sugar.

This sugar is incompletely defecated, leaving in the juice certain nitrogenous products of the beet. These products have a food value and until now have been discarded in the residue and used as fertilizer.

The sugar obtained by M. Kestner is slightly brown in color and can be used in the manufacture of chocolate and candy.

ARMAND GAUTIER

Professor Armand Gautier, one of the deans of French chemistry, has recently died at the age of 83. To him is due the discovery of nitriles, carbylamines, and ptomaines. He studied also the normal state of arsenic in the human body, and opened the way to the medical application of arsenical derivatives. He also carried on investigations on mineral waters and petroleum.

October 7, 1920

INDUSTRIAL NOTES

Experiments conducted by the Bureau of Plant Industry of the U. S. Department of Agriculture have proved the superiority of European seed-flax varieties for the north-central states.

The University of Buffalo has received a gift of $400,000 for the erection of a chemistry building, as well as anonymous gifts of $250,000 towards endowment and a library building.

The War Department has announced the sale of the Old Hickory Powder Plant at Jacksonville, Tenn., to the Nashville Industrial Corporation for $3,505,000. The Government has reserved a large amount of space at the plant for the storage of smokeless powder and other materials, as well as powder-making machinery. The Government also retains possession of the numerous concrete foundations which will assure the nucleus of a smokeless powder plant for completion and use in time of national emergency.

The Chemical Club of Philadelphia was formed at a luncheon given October 11, 1920, by the chemical jobbers and manufacturers of the city, and definite plans for the organization were formulated. Weekly luncheons are planned for the purpose of forming closer business relations among the chemical trade.

The Borden Company of New York has contributed to Columbia University $10,000 to be added to the gift previously made by it for research in food chemistry and nutrition under the direction of Prof. Henry C. Sherman. Dr. A. C. Langmuir of the class of 1893 has contributed $100 to be applied toward needed equipment in the department of chemistry.

Fire at the Butterworth-Judson Corporation plant in Newark, N. J., on September 20, completely destroyed the *p*-nitroaniline unit. Specifications for the new plant have been prepared and production is expected to begin by the first of December.

An institute for chemical and physical research has been founded in Japan at a cost of half a million pounds, subscribed by persons engaged in industry and commerce in Tokyo, Yokohama, and other towns. An annual subsidy of £200,000 has been granted by the government, and the emperor has made a personal donation of £100,000.

The office of the Technical Association of the Pulp and Paper Industry has been moved from 18 E. 41st Street to 542 Fifth Ave., New York City. The new quarters will provide opportunity for minor laboratory work, including microscopical, chemical, and physical testing of paper and fibers.

The General Electric Company has contributed $30,000 to extend the investigations of the Committee on Fatigue Phenomena of Metals of the Division of Engineering of the National Research Council, to include work on 3 per cent and 3.5 per cent nickel steel. The Engineering Foundation Board a year ago made a grant of $15,000 yearly for two years for investigations in carbon steels, the experimental work to be done at the University of Illinois under the supervision of Prof. H. F. Moore.

The United States Gypsum Co., of Chicago, has begun the construction of a plant at Sweetwater, Texas, to cost $1,000,000.

The Compressed Carbonic Co., of Baltimore, has been organized with a capital of $1,020,000, to recover 2,000,000 lbs. of carbon dioxide annually, using waste gas of the U. S. Industrial Alcohol Company at Curtis Bay. The following officers have been elected: President, A. R. Ludlow, vice president of the Air Reduction Co.; vice president and general manager, George B. Cowper.

The Emporia Potassium Phosphate Company is being organized at Emporia, Va., by Californian chemical engineers who have been instrumental in establishing the potash industry in Nebraska, to manufacture fertilizer from feldspar and phosphate rock. The process consists in fusing a combination of feldspar, phosphate rock, and a soda flux, and if the industry is developed as planned it is expected to mean revolutionizing the fertilizer industry, and rendering this country absolutely independent of German potash supplies. The product will be potassium phosphate, with an analysis of 16 per cent phosphoric acid and 6 per cent potash.

The American Cellulose and Chemical Company is to erect a large plant at Amcelle, Md., for the manufacture of artificial silk. If present plans are carried out, this will be the largest of its kind in the world.

The Crop Protection Institute has been organized by a group of scientific investigators and representatives of industrial concerns, with the advice and assistance of the National Research Council, to make a series of thorough scientific studies of the crop pests themselves and the means for improving and standardizing the materials and appliances used in fighting them. The Board of Trustees of the Institute is composed of nine scientific men representing leading scientific organizations and four representatives of manufacturing and commercial interests, with H. E. Howe, chairman of the Division of Research Extension of the National Research Council, acting as temporary secretary. The Institute will not duplicate existing efforts of government bureaus, state experiment stations or other agencies, but will introduce a more general coöperation and give special attention to filling important gaps now existing.

Twenty chemical companies were organized during the month of September 1920, with a total capitalization of $7,720,000, as compared with $36,715,000 in August and $21,475,000 in July. The total authorized capital of new companies for the first nine months of 1920 is $175,642,000 as compared with $77,436,000 in 1919, and is 50 per cent greater than the total during the year 1919.

The production of petroleum in the United States during 1919 showed an increase of about 6 per cent in quantity and 10 per cent in value over 1918, while natural gas showed a decrease of about 20 per cent in quantity.

2,000,000 tons of potash were imported to the United States from Germany in 1913, as compared with 92,000 tons for the first half of 1920.

A number of prominent steel foundries grouped for the purpose of developing and perfecting higher standards in the production of steel castings have appointed Mr. R. A. Bull, of Pittsburgh, as consulting metallurgist to devote his entire time to research work.

The manufacture of artificial fertilizer is becoming a major industry in Japan, although before the war there was only one company of any size engaged in its production. One handicap of the industry is the necessity of importing the raw materials.

The Fort Worth Acid Works, Fort Worth, Texas, is building a plant for the purpose of extracting sulfuric acid from the sludge of oil refineries. A large percentage of the acid used in the process of refining petroleum products remains in its original state, except for being rendered unavailable for further use through accumulation of particles of tar, asphalt, and other substances, but the amount of sludge from one refinery does not justify the installation of machinery for reclaiming. The Fort Worth Acid Works will obtain its raw material from refineries at Fort Worth, Dallas, Wichita Falls, Ranger, and other points.

The six-acre plant of the Barber Asphalt Company near Perth Amboy, N. J., was recently destroyed by fire with a loss of nearly $3,000,000. The four units of the plant for asphalt refining, for making roofing asphalt, for asphalt flooring products, and for asphalt paving blocks were burned, with their storehouses, only the piers along the waterfront escaping the fire. Two of the six steel tanks containing asphalt were also destroyed.

The National Malleable Castings Company has opened its new laboratory in Cleveland, Ohio, which is devoted purely to research and general investigations, the routine analytical and testing work required for works control being carried on at the various plant laboratories. The department occupies a three-story building which is equipped for work in chemistry, physics, metallography, metallurgy, and materials testing. H. A. Schwartz is manager of research, H. R. Payne, chief chemist and acting metallographer, M. M. Austin and Anna Nicholson, research chemists, A. F. Gorton, physicist, W. W. Flagle, engineer of tests, and C. A. Thornburg, chief clerk.

Experiments in the development of the turpentine industry in California during the winter season of 1919–20 have proved satisfactory. 10,000 cups were placed, and 39 bbls. of gum gathered and shipped to a refinery in San Francisco.

The Canadian Dominion Bureau of Statistics has recently issued a preliminary report in regard to the paint and varnish industry of Canada in 1918. During 1918, 45 plants were in operation, with total assets of $15,784,610, and raw materials costing $9,203,530 were used.

The United States Civil Service Commission has announced open competitive examinations for chemist at $3,000 to $5,000 a year, and associate chemist at $2,000 to $3,000 a year, to fill positions in the Chemical Warfare Service, Edgewood Arsenal, Edgewood, Md., and others requiring similar qualifications. Competitors will be rated on (1) education, training, and experience, (2) experience and training as an executive, and (3) original research work completed, and must qualify in at least one of the following optional subjects: Advanced inorganic chemistry, analytical chemistry, organic chemistry, pharmaceutical chemistry, and physical chemistry. Applications, together with unmounted photographs, must be filed by November 9, 1920, with the secretary of the Fourth Civil Service District, Old Land Office Building, Washington, D. C.

The Melbourne & Metropolitan Gas Co., of Australia, which carbonizes annually from 250,000 to 300,000 tons of coal, is considering plans for the installation of a distillation plant for the recovery of by-products of coal tar which are now wasted. The by-product plant of the Australian Gas Light Co., in Sydney, produces a revenue of $681,000 annually, treating only half of the 400,000 tons of coal used annually.

PERSONAL NOTES

Dr. Ellwood B. Spear has resigned from the faculty of the Massachusetts Institute of Technology to accept a position with the Goodyear Tire & Rubber Co., Akron, Ohio.

Mr. Robert F. Wood, for four years metallurgist with the Sandusky Foundry & Machine Co., Sandusky, O., has resigned from that position and has accepted a similar one with the Monel Metal Products Corp., Bayonne, N. J.

Mr. Harold O. Trotter who has been doing special detail work in St. Louis among physicians and dentists for Bristol-Myers Co., of Brooklyn, N. Y., is now connected with Eli Lilly & Co., Indianapolis, Ind., in their manufacturing division.

Mr. Winfield Scott has left the employ of the Goodyear Tire & Rubber Co., Akron, O., where he had charge of organic research, and has accepted a position with the Quaker City Rubber Co., Philadelphia, Pa., where he is in charge of the research department.

Mr. W. Vernon Godshall, formerly assistant professor of general, qualitative, organic, physiological and household chemistry at Miami University, Oxford, O., has accepted a similar position in physiological chemistry in the department of physiology of the University of Wisconsin, Madison, Wis., and also a position as chemist on the Interdepartmental Board for the estimation of the elimination of arsenic from patients treated with certain arsenical drugs in case of syphilis.

Mr. Max Albert, formerly chemist in charge of the branch chemical laboratory of the Bureau of Standards, Northampton, Pa., is now connected with the Newport Chemical Co. (Carrollville, Wis., operation) where he is engaged as research chemist, working on improved methods for manufacturing crystalline sodium sulfide (suitable for use in connection with production of sulfur dyes).

Mr. C. A. Browning, formerly head of the chemical department of Howe Military Academy, Howe, Ind., has recently taken a position with the People's Gas Light & Coke Co., of Chicago.

Mr. A. F. Wendler has resigned as instructor in chemical engineering at the University of Michigan, Ann Arbor, Mich., to accept a position in the test division of the engineering department of the National Aniline & Chemical Co., of Buffalo, N. Y.

Mr. Paul J. Peterson is now chief chemist with Wadsworth, Howland & Co., Malden, Mass., having formerly been connected with the North Dakota Agricultural College.

Mr. Alfred E. Galloway, a former graduate student and assistant in organic chemistry in the department of chemistry at Ohio State University, Columbus, O., has accepted a position in the organic research laboratory of the New Jersey plant of the Grasselli Chemical Company.

Mr. W. H. Keen resigned a short time ago from the Hess Steel Co., Baltimore, Md., where he held the position of tool steel manager, and has opened an office as consulting metallurgist in Newark, N. J.

Mr. P. J. Anderson has left the Root & Van Dervoort Engineering Co., East Moline, Wis., and has accepted a position with the Samson Tractor Co., Janesville, Wis., where he has charge of cupolas and mixing of grey iron and semi-steel.

Dr. Glenn S. Skinner, formerly assistant professor in organic chemistry at Oberlin College, Oberlin, O., has accepted a similar appointment in the department of chemistry at the University of Wisconsin, Madison, Wis.

Dr. G. R. Shaw, upon receiving the doctor's degree at the University of Wisconsin last June, left work there as an instructor and accepted a position with the experimental engineering laboratory of the National Lamp Works of the General Electric Co., Cleveland, Ohio.

Mr. James R. Wilson, formerly teaching fellow at the California Institute of Technology, Pasadena, Cal., is at present in the research department of the Western Electric Co., New York City.

Mr. Charles M. Hayes, a recent graduate from the Pennsylvania State College, is now connected with the National Carbon Co., Inc., Lakewood, Ohio, in the engineering department of their American Ever-Ready Works.

Mr. Harold Bedient, who has been an assistant in chemistry at Cornell University, where he was studying for his Ph.D. degree, sailed September 18 for China to take a position as professor of organic and sanitary chemistry in the Fukien University at Foo Chow, China.

Mr. Lloyd A. Hall resigned as chief chemist with John Morrell & Co., Ottumwa, Ia., to accept a similar position with the Boyer Chemical Laboratory Co., Chicago, Ill.

Dr. Edward Culmann, formerly with the Schoellkopf Works of the National Aniline & Chemical Co., Buffalo, N. Y., is now connected with the American Aniline Products, Inc., as technical director of the Lock Haven Works, Lock Haven, Pa.

Mr. Raymond E. Kirk resigned as instructor in the department of chemistry, Iowa State College, Ames, Ia., and entered upon his duties as assistant professor of general inorganic chemistry in the School of Chemistry of the University of Minnesota, Minneapolis, Minn.

Recent additions to the personnel of the Research Division, C. W. S., at Edgewood Arsenal, which is being increased rapidly to take care of the many problems which come to this Division, are as follows: **Messrs. John C. Bubb, T. E. Knapp, K. D. Ashley, Earl H. Barclay**, and **W. L. Tanner**, research chemists; **Messrs. V. T. Ellis**, and **H. L. Humphrey**, chemical engineers; **Messrs. J. C. Goshorn, Earl Otto, Benjamin Engleman, Max Berlin, J. D. Craig, E. M. Berry, H. E. Bloomsburg, R. S. Brown, Mark C. Lewis, Philip Barnhart**, and **T. E. Kendrick**, junior chemists, and **Mr. E. K. Long**, mechanical and electrical engineer. It is expected to increase the chemical and mechanical force until Edgewood has between 200 and 300 technical men engaged upon research, plant development, smoke and incendiary development, and toxicological work.

A laboratory for research on dyestuffs and explosives has been established at George Washington University, Washington, D. C., under the general supervision of **Prof. H. C. McNeil**, and in charge of **Mr. G. W. Phillips**, formerly of the Chemical Warfare Service. **Dr. C. E. Monroe**, of the National Research Council, will be consulting chemist of the laboratory.

Mr. Olin K. Smith has left the Federal System of Bakeries of America and has taken a position as industrial engineer with the Western States Portland Cement Co., of Independence, Kans.

Mr. F. H. Fish, formerly special research test assistant on the joint investigation of the fatigue of metals at the University of Illinois, Urbana, Ill., has been appointed associate professor of analytical chemistry in the Agricultural and Mechanical College of Texas, College Station, Texas.

Mr. R. H. Bullard has resigned his position with the Roessler & Hasslacher Chemical Company in order to return to Hobart College, Geneva, N. Y., as instructor in chemistry.

Mr. C. J. Overmyer, Rhodes Scholar from Michigan as of 1919, left the chemistry department of Michigan Agricultural College, East Lansing, where he was an instructor, and has sailed for Oxford, England, where he will enter Oriel College for three years' work in chemistry.

Mr. W. G. Bowers, having resigned as head of the laboratory of the State Food Commission, Fargo, N. D., recently accepted an appointment as head of the department of chemistry in the Colorado State Teachers' College at Greeley, Col.

Mr. H. H. Brown, formerly connected with the Bureau of Chemistry, Department of Agriculture, where he was in charge of the chemical investigations on the cause and prevention of dust explosions, is at present employed by the Pejepscot Paper Co., Brunswick, Maine, to establish a chemical research laboratory and to investigate chemical problems connected with the manufacture of paper and the utilization of waste products.

Mr. L. D. Vorce resigned as works manager with the Canadian Salt Co., to take up active duties with the Precision Instrument Co., of Newark, N. J., of which concern he is vice president.

Mr. W. W. Hambly, until recently connected with E. I. du Pont de Nemours & Co., has secured a position in the production department of the General Electric Co., Schenectady, N. Y.

Mr. R. B. Arnold has given up his work as consulting chemical engineer at Richmond, Va., and has become vice president, in charge of manufacture, of the Delion Tire & Rubber Co., of Baltimore, Md.

Mr. Ralph B. Hammond, formerly research chemist at the Mathieson Alkali Works, Inc., Niagara Falls, N. Y., has resigned from that position to become division superintendent of the Acheson Graphite Company, of the same city.

Mr. H. B. Pulsifer, formerly of the Montana State School of Mines, is now assistant professor of metallurgy at Lehigh University, Bethlehem, Pa.

Mr. George D. Chamberlain recently changed his business connections from metallurgical engineer for the Heppenstall Forge & Knife Co., Pittsburgh, Pa., to assistant general superintendent of the Standard Seamless Tube Co., Ambridge, Pa.

Mr. Lauren H. Ashe has resigned as chief chemist and production manager of the Capital City Products Co., Columbus, Ohio, to become assistant general manager of the Ko-Ko-Mar Co., of Cleveland, Ohio.

Mr. Chas. L. Wiswall recently accepted a position with the Perth Amboy Chemical Works, Perth Amboy, N. J., as chemical engineer, his former position being production manager of the Vulcan Detinning Co., Sewaren, N. J.

Mr. E. B. Cordon upon graduating from the University of North Carolina last June accepted a position as a chemist in the plant laboratories of the Pratt and Lambert Varnish Co., Buffalo, N. Y.

Dr. Waldemar T. Schaller has severed his connection with the Great Southern Sulphur Co., Inc., of New Orleans, La., and has returned to the U. S. Geological Survey, Washington, D. C.

Mr. Fred S. Mulock, formerly operating superintendent of the U. S. Bureau of Mines at the U. S. Government Experiment Station, Petrolia, Texas, is now in the research department of the U. S. Smelting, Refining, and Mining Co., Boston, Mass., and is at the same time connected with the U. S. Bureau of Mines as consulting mechanical engineer.

Dr. M. C. Teague resigned as gas chemist at the Pittsburgh Station of the U. S. Bureau of Mines to accept the position as research chemist for the U. S. Rubber Co., New York City.

Mr. Paul D. Watson, a graduate last June in the chemical engineering course at the University of Pittsburgh, is now assistant chemist with the General Chemical Co., at their Laurel Hill Laboratories, L. I., N. Y.

Mr. M. C. Burt, formerly connected with the Aetna Explosive Co., has been put in charge of the Bridgeport Works of the Remington Typewriter Co., Bridgeport, Conn., where carbon paper and typewriter ribbons are manufactured.

Mr. Reginald K. Pierce, treasurer of the Semet-Solvay and the Kentucky Solvay companies, was killed recently in an automobile accident.

Mr. Harry I. Johnson has been appointed director of the new chemistry department at Roanoke College, Salem, Va., having resigned as assistant professor of chemistry at N. C. State College of Agricultural & Engineering, West Raleigh, N. C.

Mr. Ralph A. Gould and **Mr. Bryant S. Drake** announce their association from August 1, 1920, as a partnership under the firm name of Gould & Drake, chemical engineers, with offices in San Francisco, Cal.

Mr. Thomas P. Shields has left Hoover & Strong, Inc., Buffalo, N. Y., where he was superintendent, to take a position as technical director of Wendall & Co., manufacturing jewelers and refiners, New York City.

Dr. Roland Neal, professor of chemistry at the College of the Pacific, San Jose, Cal., since 1910, has been appointed to the professorship of chemistry in Drury College at Springfield, Mo.

Mr. Thomas E. Comerford, formerly employed as chemist by the Aetna Explosive Co., at their Fayville, Ill., plant, is at present employed in a similar capacity by the Oldbury Electrochemical Co., Niagara Falls, N. Y.

Mr. Fred W. Geise, for the past three years connected with the U. S. Department of Agriculture, Bureau of Plant Industry, Washington, D. C., with temporary station at University of Chicago, Hull Botanical Laboratories, Chicago, Ill., is now associate plant physiologist with the Virginia Truck Experiment Station, Norfolk, Va.

Mr. C. H. Kidwell resigned recently as chief of the Quality of Water Division of the Water Resources Branch of the U. S. Geological Survey, Washington, D. C., to accept a position with the Solvay Process Co., Syracuse, N. Y.

Mr. Robert H. Currie, formerly of the main office chemical staff of the du Pont Co., Wilmington, Del., has accepted a position with the Acheson Graphite Co., Niagara Falls, N. Y., as superintendent of the lubricant works.

Mr. Claude E. McLean resigned his position as first assistant chemist in the Memphis Laboratory of the Union Seed & Fertilizer Co., to accept a position as chemist in charge of a laboratory for the Osage Cotton Oil Co., Muskogee, Okla.

Mr. H. B. Corbett has severed his connections with the U. S. Public Health Service as sanitary bacteriologist, and has joined the forces of the H. A. Metz Laboratories, New York City, where he will work in the biological testing division.

Mr. Paul Moore, now director of the Information Bureau of the War Trade Board, became Secretary of the Division of Research Extension, National Research Council, on or about October 1, and will devote his efforts to the promotion of research with special reference to the industries.

Mr. Carl G. Hinrichs, a graduate of the St. Louis College of Pharmacy, has been elected associate professor of chemistry of that institution.

Dr. H. E. Wells, formerly professor of chemistry at Washington and Jefferson College and a Captain in the Chemical Warfare Service, U. S. A., has been appointed professor of chemistry at Smith College, Northampton, Mass.

Mr. F. H. Tucker has severed his relations as associate chemist of the Bureau of Standards, Washington, D. C., to become chemist in the research laboratories of the Chile Exploration Co., New York City.

Mr. Geoff A. Saeger resigned as chief chemist for the Lehigh Portland Cement Co., New Castle, Pa., to accept a similar position with the Bessemer Limestone & Cement Co., Bessemer, Pa.

Mr. Benjamin R. Jacobs recently announced his resignation from the Bureau of Chemistry, Washington, D. C., having accepted the directorship of the National Cereal Products Laboratories, with offices in the above city.

Dr. F. Hastings Smyth resigned as secretary of the Clinton Metallic Paint Co., Clinton, N. Y., to accept a position on the staff of the Geophysical Laboratory of the Carnegie Institution of Washington.

Mr. F. D. Haskins who was formerly instructor in chemistry at Washington University, St. Louis, Mo., has been appointed assistant professor of chemistry at Mercer University, Macon, Ga.

Mr. G. H. Montillon, instructor of chemical engineering at the University of Wisconsin, Madison, Wis., for the year 1919–1920, has resigned, and is now assistant professor of chemical engineering at the University of Minnesota, Minneapolis, Minn.

Dr. Arthur M. Buswell, formerly instructor in sanitary chemistry at Columbia University, has been appointed chief of the Illinois State Water Survey, and associate professor in sanitary chemistry at the University of Illinois.

Dr. Carl L. Alsberg, chief of the Bureau of Chemistry, was elected president of the Association of American Dairy Food and Drug Officials at their recent convention held in St. Louis.

Mr. Charles W. Cuno, formerly professor of chemistry at Yankton College, Yankton, S. D., has accepted the position of assistant professor of chemistry in Washington University, St. Louis, Mo.

Mr. C. W. Botkin, associate professor of chemistry at the Colorado School of Mines, has resigned to accept a position as research chemist for the American Shale & Petroleum Co., of San Francisco, Cal. The research work, however, will be conducted at the Colorado School of Mines in Golden, Col.

Mr. Harold N. Hermann recently joined the engineering staff of the Mantius Engineering Co., Inc., New York City, having previously been associated with the Eflorose Sugar Co., Carthage, Ohio, as chemist.

Mr. H. B. Riffenburg, assistant professor of chemistry and chemical engineering, at Texas Agricultural and Mechanical College, College Station, Texas, recently resigned to accept a position as junior chemist in the Quality of Water Division of the Water Resources Branch of the U. S. Geological Survey, Washington, D. C.

Mr. R. A. Watson, formerly with the Gem Yarn & Dye Works of Central Falls, R. I., has become teacher of dyeing in the Philadelphia Textile School, Philadelphia, Pa.

Mr. Raymond A. Heindl has resigned as assistant chemist with the Aluminum Company of America to accept the position of chemist with the National Abrasive Co., Niagara Falls, N. Y.

Dr. Rodney B. Harvey resigned as plant physiologist, Bureau of Plant Industry, Washington, D. C., to accept the position of assistant professor in plant physiology at the University of Minnesota, and assistant plant physiologist in the Minnesota Experiment Station. Dr. Harvey will still be retained by the Bureau of Plant Industry as collaborator under a coöperative arrangement.

Mr. John F. McBride who was formerly in the research department of the National Aniline & Chemical Co., studying methods of production of certain dyestuffs and intermediates, has entered the department of chemistry of the University of Chicago where he will begin research for the Ph.D. degree in organic chemistry.

GOVERNMENT PUBLICATIONS

By Nellie A. Parkinson, Bureau of Chemistry, Washington, D. C.

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

UNITED STATES TARIFF COMMISSION

Barytes, Barium Chemical, and Lithopone Industries Including Costs of Production, 1919. Tariff Information Series No. 18. 90 pp. Paper, 15 cents. Issued September 1920.

The Crude Botanical Drug Industry. Tariff Information Series No. 19. 69 pp. Paper, 10 cents. Issued September 1920. This pamphlet presents a discussion of the crude botanical drug industry, with special reference to those foreign and domestic articles of chief importance in the drug trade. The report is divided into two parts and an appendix. (1) Drugs are defined and classified, and the world trade, production, and consumption of these articles are discussed; a brief review of tariff treatment and policy is also presented. (2) This chapter classifies drugs according to their geographical source, and is chiefly concerned with the principal imported articles and those which have been or may probably be cultivated commercially in the United States. (Appendix.) The portions of the Tariff Act of 1913 referring to drug products are cited.

PUBLIC HEALTH SERVICE

Acid Burns on Hands of Solderers. Experience at the Curtis Bay General Ordnance Depot, South Baltimore, Md. H. W. Keatley. Public Health Reports, **35**, 2161–3. The soldering process, the problem it presents, the causes of the burns, and preventive measures are described.

Methods of Increasing the Efficiency of Rural Sanitation. T. J. Robinson. Public Health Reports, **35**, 2200–2.

"Fake" Orange Beverages. Public Health Reports, **35**, 2204–5. Attention is called to the fact that these "fake" preparations are generally lacking in the organic acids and the vitamines which give medicinal value to the genuine orange juice.

The Effect of Shaking Alkalinized Aqueous Solutions of Arsphenamine and Aqueous Solutions of Neoarsphenamine in the Presence of Air. G. P. Roth. Public Health Reports, **35**, 2205–10. Shaking alkalinized aqueous solutions of arsphenamine or aqueous solutions of neoarsphenamine in the presence of air renders them highly toxic, as shown by intravenous administration to white rats. The increase in toxicity caused by such shaking is presumably due to the oxidation of these compounds to *p*-oxyphenylarsenoxide, inasmuch as shaking a solution of neoarsphenamine in the absence of air does not increase the toxicity of such a solution. The conclusion drawn from the investigations is that the toxicity of aqueous solutions of neoarsphenamine is greatly influenced by the manner in which they are prepared for administration.

Quantitative Studies in Chemotherapy. I. The Trypanocidal Action of Arsenic and Antimony Compounds. Carl Voegtlin and H. W. Smith, with the coöperation of M. M. Crane, K. D. Wright and M. A. Connell. Public Health Reports, **35**, 2264–73. A method for the rapid and accurate determination of the trypanocidal power of drugs is recommended. A sharply defined minimum effective dose is observed, below which the drug has no appreciable effect upon the parasites of infectious diseases. Arsphenamine and neoarsphenamine have to be oxidized in the body before they can act upon the parasites.

Treatment and Disposal of Sewage. Brief Descriptions of Methods, Processes, and Structures Used in the Treatment and Disposal of Sewage in the United States, with Bibliography. H. B. Hommon, J. K. Hoskins, H. W. Streeter, R. E. Tarbett and H. H. Wagenthals. Reprint No. 580 from Public Health Reports. 36 pp. Paper, 10 cents. 1920.

Prevention of Stream Pollution by Dye and Intermediate Wastes. E. J. Casselman. Reprint No. 581 from Public Health Reports. 23 pp. 1920.

GEOLOGICAL SURVEY

Mineral Resources of the United States in 1919. Preliminary Summary. Introduction by G. F. Loughlin. Statistics assembled by M. B. Clark. 128 pp. Issued September 8, 1920. Statistics of mineral production in the United States for 1919 reflect the reaction from intensive production for war purposes and the unsettled state of industry in general. Production of special "war minerals" rapidly subsided, although not to its pre-war status. The principal decline was due to diminished production of coal and the major metals. The total value of all mineral products in 1919 was about $4,653,700,000, 16 per cent less than in 1918. The value of metal products decreased 36 per cent, but it is estimated that the value of mineral fuels and other nonmetallic products decreased only 3 per cent due to higher prices in 1919. A comparison of production in 1913 and 1919 indicates an increase of 86 per cent in total value due to increase in price. With the exception of the "war minerals" most commodities were below normal in output. Marked increases in production are to be expected in 1921 and succeeding years until normal output is reached.

Cobalt, Molybdenum, Nickel, Titanium, Tungsten, Radium, Uranium, and Vanadium in 1917. F. L. Hess. Separate from Mineral Resources of the United States, 1917, Part I. 61 pp. Published August 31, 1920. The various metals are treated separately, with the exception of radium, uranium, and vanadium, which are handled as one group, and in nearly every instance general conditions, production, uses, prices, imports and exports are described.

Gold, Silver, Copper, Lead, and Zinc in Colorado in 1918. C. W. Henderson. Mines Report. Separate from Mineral Resources of the United States, 1918, Part I. 57 pp. Published September 2, 1920. The total value of the gold, silver, copper, lead, and zinc produced in Colorado in 1918 was $34,160,172, a decrease of 19 per cent from the value in 1917.

Petroleum in 1918. E. R. Lloyd. Separate from Mineral Resources of the United States, 1918, Part II. 201 pp. Published September 20, 1920. The year 1918 witnessed the organization of the industry on a war basis under the direction of the United States Fuel Administration, a quickening of activity in all phases of the industry, and an active coördination of all its branches in a complete and unified organization for the one purpose of supplying petroleum products for the necessary operations of the United States and the allied nations in winning the war. The one region of outstanding interest was northern central Texas. The quantity of crude petroleum produced in the United States in 1918 aggregated 355,927,716 bbls. of 42 gal. each, an increase of more than 6 per cent over the former maximum yield of 335,315,601 bbls. in 1917.

Natural-Gas Gasoline in 1918. E. G. Sievers. Separate from Mineral Resources of the United States, 1918, Part II. 35 pp. Published September 22, 1920. The quantity of natural-gas gasoline produced in 1918 was about 30 per cent greater than that produced in 1917; the increase in 1917 over 1916 was 110.5 per cent. The total quantity of raw gasoline recovered in 1918 was 282,535,550 gal. The outstanding feature of the industry in 1918 was the large increase in production by the compression plants in Oklahoma.

Arsenic, Bismuth, Selenium, and Tellurium in 1919. J. M. Hill. Separate from Mineral Resources of the United States, 1919, Part I. 9 pp. Published September 16, 1920. Statistics are given showing the production, imports, exports, and price of arsenic and bismuth. In the case of selenium, statistics showing the production, imports, consumption, and price are given. There was a small demand for tellurium in 1919, but the stocks of tellurium are apparently large as compared with the annual consumption.

A Deposit of Manganese Ore in Wyoming. E. L. Jones, Jr. Bulletin 715-C. Separate from Contributions to Economic Geology, 1920, Part I. 3 pp. Published September 18, 1920.

Some Deposits of Manganese Ore in Colorado. E. L. Jones, Jr. Bulletin 715-D. Separate from Contributions to Economic Geology, 1920, Part I. 12 pp. Published September 17, 1920.

Geology of the Yellow Pine Cinnabar-Mining District, Idaho. E. S. Larsen and D. C. Livingston. Prepared in coöperation with the Idaho State Bureau of Mines and Geology. Bulletin 715-E. Contributions to Economic Geology, 1920, Part I. 11 pp. Published September 15, 1920.

Deposits of Iron Ore near Stanford, Montana. L. G. Westgate. Bulletin 715-F. Contributions to Economic Geology, 1920, Part I. 8 pp. Published September 16, 1920.

Surface Water Supply of the United States, 1917. Part II. South Atlantic Slope and Eastern Gulf of Mexico Basins. N. C. Grover, G. C. Stevens, and W. E. Hall. Water-Supply Paper 452. 92 pp. Paper, 10 cents.

Surface Water Supply of the United States, 1918. Part IV. St. Lawrence River Basin. N. C. Grover, W. G. Hoyt, A. H. Horton, C. C. Covert and C. H. Pierce. Prepared in coöperation with the states of Wisconsin, New York, and Vermont. Water-Supply Paper 474. 110 pp. Paper, 15 cents.

BUREAU OF MINES

Monthly Statement of Coal-Mine Fatalities in the United States, June 1920. W. W. Adams. 13 pp. Paper, 5 cents.

BUREAU OF STANDARDS

Permeability of Rubber to Gases. J. D. Edwards and S. F. Pickering. Scientific Paper 287. 36 pp. Paper, 10 cents. 1920. The permeability of rubber compounds varies with the composition. The relative permeability of rubber to some common gases is shown in the following summary:

Gas	Relative Permeability (Hydrogen = 1)
Nitrogen	0.16
Air	0.22
Argon	0.26
Oxygen	0.45
Helium	0.65
Hydrogen	1.00
Carbon dioxide	2.9
Ammonia	8.0
Methyl chloride	18.5
Ethyl chloride	200.0

Recommended Specifications for Volatile Mineral Spirits for Thinning Paints. Prepared and recommended by the United States Interdepartmental Committee on Paint Specification Standardization, July 26, 1920. Circular 98. 6 pp. Issued August 24, 1920. These specifications apply only to petroleum distillates, known as mineral spirits. General specifications are outlined and directions are given for the detection and removal of separated water, sampling, laboratory examination, and basis of purchase.

The Two Common Failures of the Clark Standard Cell. E. C. McKelvy and M. P. Shoemaker. Scientific Paper 390. 12 pp. Paper, 5 cents.

Automatic Apparatus for Intermittent Testing. G. W. Vinal and L. M. Ritchie. Technologic Paper 171. 7 pp. Paper, 5 cents.

DEPARTMENT OF AGRICULTURE

The Process of Ripening in the Tomato, Considered Especially from the Commercial Standpoint. C. E. Sando. Department Bulletin 859. 38 pp. Paper, 10 cents. Issued September 7, 1920.

The Castor-Oil Industry. J. H. Shrader. Department Bulletin 867. 40 pp. Issued September 3, 1920.

Experiments on the Toxic Action of Certain Gases on Insects, Seeds, and Fungi. I. E. Neifert and G. L. Garrison. Department Bulletin 893. 16 pp. Paper, 5 cents. Issued September 8, 1920.

Proceedings of Conference of Men Engaged in Grain Dust Explosion and Fire Prevention Campaign Conducted by the United States Grain Corporation in Coöperation with the Bureau of Chemistry. 159 pp. Copies of this publication may be obtained upon application to the Bureau of Chemistry.

Articles from the Journal of Agricultural Research

Investigations in the Ripening and Storage of Bartlett Pears. J. R. Magness. 19 (August 16, 1920), 473–500.

COMMERCE REPORTS—SEPTEMBER, 1920

Germany plans to release 30,000 to 50,000 tons of **nitrogen**, which has been made by the Haber process from air, to be exported duty-free. The prices charged to German domestic fertilizer consumers will be reduced by the use of the receipts of sales made abroad. (P. 1062)

Bituminous limestones (asphalt) are being distilled in Palestine and Syria to meet the pressing demand for lubricating oil. (P. 1077)

The Italian production of **copper sulfate** in 1920 it is estimated will be ample to supply domestic needs. (P. 1099)

The outlook for the London **tin** market is said to be more optimistic than for some time past. (Pp. 1105–6)

The Alsatian **potash** industry is reviewed. The production for 1920 is estimated at 1,320,000 metric tons of crude salts; for 1921, 2,040,000 metric tons; and for 1922, 2,340,000 metric tons. Of the amount produced, about 33 per cent is utilized in France and 66 per cent is exported. (Pp. 1108–12)

The production of **santonin** in Russia is reviewed. (P. 1113)

Recent researches have shown that the amount of **lignite** existing in the subsoil of Italy in the deposits explored up to the present time may be estimated at about 270,000,000 tons. (P. 1114)

The Government will not exercise the option extended by the Reparation Commission upon impounded stocks of **chemical drugs** of German manufacturers or upon stocks of chemical drugs manufactured during the months January 1920 to June 1920, inclusive. It will, however, retain its right to participate in allotments from future daily production of chemical drugs which may be manufactured in Germany during the next four and one-half years. (P. 1126)

The United States Government has decided to exercise its option upon German impounded **dyestuffs**, and has authorized the Textile Alliance, Inc., to purchase these stocks in the interest of the American consumer. No dyes from these stocks may be imported which are either manufactured here, or for which suitable substitutes are manufactured here, on reasonable terms as to price, quality, and production. (Pp. 1134–5)

Attention is called to the importance of the **mineral resources** of the South Pacific Islands. Chrome, cobalt, and nickel are found in abundance; antimony, mercury, silver, lead, and copper have also been found. Nickel ore, nickel matte, and chrome ore constitute the chief exports. (P. 1139)

The cultivation of the **guinea oil palm** is being encouraged in the Philippine Islands. It produces two classes of oil, one from the fruit itself and one from the kernel. The cultivation of this palm is said to be more profitable than that of coconuts. (P. 1144)

It is estimated that approximately 44.4 per cent of the **paper** produced in the former Austro-Hungarian Empire in 1913 was manufactured in the present territory of Czechoslovakia. From April 15 to June 30, 1920, paper and pulp products held the first place among the Czecho-Slovak exports. (Pp. 1153–6)

Statistics are given showing the imports and exports of **vegetable oil** and vegetable-oil material by Japan during 1917, 1918, and 1919. (Pp. 1174–5)

Indications of **oil** are reported in Guppeland, Victoria, where the formation of the country is said to be similar to that of other oil-bearing centers. Bituminous shale, natural gas, mica, copper, and other valuable minerals are also believed to be present in this region. (P. 1180)

Important deposits of **barytes** are now being developed in South Australia. Certified analysis has shown this product to be of unsurpassed purity. (P. 1181)

According to a recent agreement, Belgium will receive for two years 240,000 tons of Australian **zinc ore.** (P. 1197)

Statistics are given showing the imports of **rubber** into Canada during the three years ended March 31, 1920. Since there is only one firm in British Columbia interested in the manufacture of rubber goods there is an excellent opportunity for American-made products. (Pp. 1208–12)

The **petroleum** industry of Mexico, which ranks second in oil production and has the greatest demonstrated supply, is reviewed in detail. From the following table it will be seen that the Mexican production of oil has multiplied more than three times in the last seven years. The production is reported in barrels of 42 gallons.

Year	Mexico Bbls.	United States Bbls.	World Bbls.
1913	25,902,439	248,446,230	384,667,550
1914	21,188,427	265,762,535	399,667,168
1915	32,910,508	281,104,104	426,370,894
1916	39,817,402	300,767,158	459,433,319
1917	55,292,770	335,315,303	505,362,367
1918	63,828,327	355,927,716	514,729,354
1919	87,359,533	377,719,000	......

(Pp. 1213–31)

The total production of **pig iron** in Canada during the first half of 1920 was 502,667 short tons, as compared with a production of 524,977 tons during the first half of 1919, and 392,804 tons during the second half of 1919. (P. 1241)

Statistics are given showing the imports and exports of **vegetable oil** and vegetable-oil material by Spain during 1917, 1918, and 1919. (P. 1251)

The **artificial silk** trade of the United States, which is rapidly developing an absolutely new domestic industry, is reviewed. (Pp. 1252–7)

The following table gives comparative statistics of the export of **rubber** from the Straits Settlements:

Month	1918 Tons	1919 Tons	1920 Tons
January	4,302	14,404	13,125
February	2,334	15,666	17,379
March	8,858	20,908	5,931
April	6,584	10,848	15,720
May	13,587	15,845	15,617
June	6,515	5,059	11,663
July	1,978	7,818	10,773
Total	44,158	90,543	90,208

(P. 1290)

Statistics are given of the imports and exports of **vegetable oil** and vegetable-oil material by Switzerland during 1917, 1918, and 1919. (Pp. 1300–1)

The Chemical Works Department of Glasgow Corporation proposes to manufacture chemicals from **gas residuals.** The principal chemicals to be manufactured will be motor benzene, pure benzene, toluene, solvent and heavy naphthas, and carbonic acid. The advisability of making dyes and intermediates will also be considered. (P. 1312)

The French commission charged with the study of all matters relating to the production and utilization of **substitutes for coal** in its first annual report urges the French government to occupy itself with research work in France and its colonies and favor private initiative engaged in the work of prospecting and drilling for oil. The government is also urged to develop the production of peat and lignite, to take an inventory of the wood resources of France, and to encourage the utilization of certain classes of wood for fuel. (P. 1315)

The year 1919 was unfavorable for the Swedish **dye industry.** (P. 1316)

Of the total amount of **aniline dyes** imported into China during 1919, over 50 per cent came from the United States, about 25 per cent from Japan, the remainder being of French and other origin. Prior to the war German dyes practically monopolized the China market. Some of the dyes sell for such ridiculously low prices that it seems safe to assume that they are imitations. (Pp. 1322–3)

A new **camphor** producing center is reported at Burma. (P. 1324)

The available supply of **ferromanganese** in India is seriously affected because of the shortage of many thousands of wagons on the Indian railways and the congested condition of traffic. (Pp. 1324–5)

A good market for American **dyes** is reported in Western Greece. The colors most desired are black, navy blue, brown, green, red, and orange. (P. 1331)

Statistics are given showing the imports and exports of **vegetable oil** and vegetable-oil material by British India during the fiscal years ending March 31, 1918, 1919, and 1920. (P. 1336)

The stocks of the German firms which in pre-war times controlled the Serbian trade in **aniline dyes** have been taken over by a Serbian company with a practical monopoly of the trade for the time being. (P. 1339)

It is believed that the great number of **chromium ore** deposits in Russia and their nearness to metallurgical centers will give them much importance when conditions are again normal and proper methods of exploitation are adopted. The United States is the most important consuming country, using over 50 per cent of the world's production. (P. 1342)

Statistics are given showing the imports and exports of **vegetable oil** and vegetable-oil material by France during 1917, 1918, and 1919. (Pp. 1353–5)

Specifications of the special apparatus used in testing **Portland cement** in Chosen are given. (Pp. 1358–9)

A board of administration for the promotion of the German **textile** industries on a scientific basis has been created. The purposes of the board are the scientific investigation of domestic and foreign vegetable fibers, the question of substitutes, the search for and utilization of vegetable fibers grown in Germany which, up to the present time, have not been used, and the improvement in the production of artificial fibers and substitutes. (P. 1364)

At a recent meeting of the stockholders of the Potash Syndicate at Wintershall the stockholders demanded that, in order to be sure of regular export orders, **potash** prices should be reduced, especially for America. (P. 1364)

The mineral production in South Africa is reviewed, and a summary is given of the mineral production for May 1920. (P. 1366)

A heavy increase is reported in the price of **gasoline** in the United Kingdom. Gasoline substitutes are expected to play an important part in supplying fuel for motors until the potentially rich fields commence production and others become accessible. (P. 1373)

Possible developments in Russia's **chemical industry** and trade are noted. It is anticipated that the dye and wood distilling industries will do business on a larger scale. The operation of factories for the treatment of fats will be delayed by the shortage of fats. The most important item of the chemical industry in Russia is artificial fertilizers. A project is under way to obtain nitric acid from the air. (Pp. 1397–1401)

Specifications are given for **Portland cement** used by the Victorian Public Works Department and the Melbourne Board of Works. (P. 1402)

Statistics are given showing the imports and exports of **vegetable oil** and vegetable-oil material by the United Kingdom during 1917, 1918, and 1919. (Pp. 1413–5)

The **juice** of the **nipah palm** is said to contain 12 per cent of sugar. Experiments have shown that the process of extraction is commercially possible. In British North Borneo there are about 300,000 acres of nipah palm. In the Philippines, alcohol has been obtained from this palm for use as a beverage and as a fuel. (P. 1416)

Considerable deposits of **rock salt** have been discovered in New Greece. (P. 1457)

The **rubber** and rubber goods markets in Latin America are reviewed. (Pp. 1476–8)

Statistics are given on the imports and exports of **vegetable oil** and vegetable-oil material by the Dutch East Indies during 1917, 1918, and 1919. (Pp. 1491–2)

The **iron ore** resources of the world are reviewed. (Pp. 1498–1507)

SPECIAL SUPPLEMENTS ISSUED IN SEPTEMBER

FRANCE—*7b*
PORTUGAL—*14a*
LITHUANIA—*16a*
SPAIN—*18a*
SWITZERLAND—*20a*
BRITISH WEST INDIES—*25b*
DOMINICAN REPUBLIC—*29a*
DUTCH WEST INDIES—*30a*
STRAITS SETTLEMENTS—*59a*
BRITISH SOUTH AFRICA—*69a*
VIRGIN ISLANDS OF THE UNITED STATES—*77a*

STATISTICS OF EXPORTS TO THE UNITED STATES

- LONDON—(Pp. 1350–1)
  - Rubber
  - Hides
  - Drugs and chemicals
  - Tin
  - Leather
  - Lead
  - Creosote oil
  - Nitrogenous fertilizer
  - Copper
  - Aluminium
  - Dynamite glycerol
  - Gums
  - Linseed oil
- CEYLON—(P. 1325)
  - Rubber
- MADAGASCAR—(P. 1179)
  - Beeswax
  - Graphite
- GREAT BRITAIN (Pp. 1093–4)
  - Salt (not table)
  - Hides (undressed)
  - Cement (calcareous)
  - Iron
  - Steel
  - Lead manufactures
  - Tin
  - Ammonium sulfate
  - Bleaching powder
- CANADA—(P. 1469)
  - Paper
  - Chemical pulp
  - Mechanical pulp
- PORTUGAL—(P. 1071)
  - Rubber
- TRINIDAD—(P. 1338)
  - Tonca beans
- SHANGHAI (P. 1067)
  - Antimony
  - Albumin
  - Camphor
- ITALY—(P. 1488)
  - Citrate of lime
- PALERMO—(P. 1407)
  - Citric acid
  - Tartaric acid
  - Sulfur oil
- NETHERLANDS EAST INDIES—(P. 1375)
  - Quinine
  - Cinchona bark
- PHILIPPINE ISLANDS—(P. 1144)
  - Guinea oil

BOOK REVIEWS

Practical Standardization by Chemical Assay of Organic Drugs and Galenicals. By A. B. LYONS, F.C.S. 397 pp. Nelson, Baker & Co., Detroit, 1920. Price, $3.50.

No other book covers quite the same field as this, and for years there has been a dearth of properly compiled information such as it presents. Twenty-two years ago Dr. Lyons published a rather brief "Handbook of Chemical Assay of Drugs and Galenicals," which has served as the basis for this much more elaborate and comprehensive work. Dr. Lyons has been intimately in touch with the assay of drugs and medicinal substances for a great portion of his life, and is well fitted to speak with authority on the subject whereof he writes. The present volume goes much farther than the determination of alkaloidal or glucosidal constituents in drugs, and embraces also such subjects as the determination of solvents used in medicinal products; the valuation of some of the nonpotent vegetable drugs, for example, acacia, capsicum, licorice, mustard, etc.; a very brief statement of the essential characteristics of those volatile oils most frequently used in medicinal compounds, and methods for determination of the chief constituents of a few of the most important; approved methods of assay for some 40 or 50 organic medicinal substances, chiefly synthetic, for example, acetanilide, antipyrin, benzaldehyde, camphor, chloroform, ethyl nitrite, glycerophosphates, iodoform, lecithins, nitroglycerin, phenol, etc.; a brief chapter on the estimation of starch, cane sugar, lactose and glucose; one upon the assay of diastase, pancreatin, papain and pepsin, and some concise information on the chemical assay of suprarenal and thyroid glands.

Within so small a volume it would seem impossible to incorporate adequate information regarding the detailed testing of so large a number of substances, but the various assay methods are efficiently condensed and frequent journal references are given to the original source of information.

The book deserves a place in every laboratory having to do with the assay of medicinal substances, and, while primarily written for the experienced chemist, it will surely prove an excellent handbook in connection with teaching of drug analysis.

Chemists of experience in this particular line of work will not always agree with the author as to the preferred method of assay, but the entire field has been dealt with in a broad-minded way, and methods are given to suit varied conditions and different ideas.

The book itself is of convenient size, of good typographical makeup and contains comparatively few typographical errors. Each paragraph is introduced by black-faced type, indicating its contents, and is also numbered for convenience of indexing and cross reference. Last, but not least in a book of this kind, it possesses a good index.

FRANK O. TAYLOR

Les Colloides Métalliques. Propriétés et Préparations. By PAUL BARY, Consulting Engineer, formerly Director of the School of Physics and Chemistry and of the Central Laboratory of Electricity. viii + 95 pp., 13 figures, 6 tables. Dunod, Paris, 1920. Price, 5 fr. 50.

The subject matter of this book is somewhat broader in scope than is indicated by the title; for, in addition to the metals such as Pt, Au, Ag, Cu, etc., C, P, S, Se, and Te are also dealt with in detail. The book is divided into four chapters. Chapter I, comprising 29 pages, is devoted to the discussion of the fundamental properties of suspensoids. In this limited space the treatise is necessarily elementary and incomplete. On the contrary, Chapters II and III, dealing with the methods of chemical and electrical colloidation, have been written with a very considerable effort toward comprehensive thoroughness. Chapter IV, on applications, contains a review of the many uses to which colloidal metals have been put. Their employment as catalytic agents is especially well dealt with, and the six pages of bibliography on this important phase of the subject will doubtless prove of great value to the chemist. The entire work is written in a pleasing scientific style devoid of flourish or circumlocution, and is well up to date.

ELLWOOD B. SPEAR

NEW PUBLICATIONS

Catalog: Chemical Engineering Catalog. 1450 pp. Price, $7.50, postpaid (Leasing privilege $2.00; in foreign countries, $3.50). The Chemical Catalog Co., Inc., New York.

Chemical Industry: L'Appareillage Mâcanique des Industries Chimiques. A. Parnicke. French translation by E. Campagne. 356 pp. Illustrated. Price, 34 fr. Dunod, Paris.

Chemical Reactions, Their Theory and Mechanism. K. George Falk. 220 pp. Price, $2.50. D. Van Nostrand Co., New York.

Dyes: A Text-Book of Dye Chemistry. Georg von Georgievics and Eugène Grandmougin. Translated and revised from 4th German edition. 560 pp. Price, 30s. net. Scott, Greenwood & Son, London.

Fertilizers: Chemical Fertilizers and Parasiticides. S. Hoare Collins. 285 pp. Illustrated. (Industrial Chemical Series.) Price, $3.50. D. Van Nostrand Co., New York.

Handbook: Chimie. Émile Javet. 426 pp. Price, 8 fr. Dunod, Paris.

Handbook: Metallurgie. David Levat. 336 pp. Illustrated. Price, 8 fr. Dunod, Paris.

Hydraulic Tables. Gardner S. Williams and Allen Hazen. 3rd ed., revised. 115 pp. 6 × 9. Price, $2.00. John Wiley & Sons, Inc., New York.

Manual of Chemical Plant. S. S. Dyson. 2nd ed. Price, £2 5s. net. The Dover Printing and Publishing Co., Ltd., Dover, England.

Metallurgy: Lecons de Sidérurgie. Anglès d'Auriac. 714 pp. Illustrated. Price, 74 fr. Dunod, Paris.

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Minerals: Die Technisch Wichtigen Mineralstoffe: Ubersicht ihres Vorkommens und ihrer Entstehung. K. Mieleitner. Illustrated. Price, M 19.40. R. Oldenbourg, München and Berlin.

Modern Electroplater. Kenneth M. Coggeshall. 276 pp. Illustrated. Price, $3.00. The Norman W. Henley Publishing Co., New York.

Resins: Gewinnung und Verarbeitung von Harz und Harzprodukten. G. Austerweil and J. Roth. Illustrated. Price, M 16.25. R. Oldenbourg, München and Berlin.

Theoretical Chemistry: Einfuhrung in die Mathematische Behandlung de Naturwissenschaften. W. Nernst and A. Schönflies. Illustrated Price, M 23.75. R. Oldenbourg, München and Berlin.

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Arsenic: The Manufacture of White Arsenic. E. C. Williams. *Engineering and Mining Journal*, Vol. 110 (1920), No. 14, pp. 671–673.

Artificial Silk Industry in Japan. K. Yamada. *The Chemical Age* (London), Vol. 3 (1920), No. 65, p. 282.

Briquets: Good Briquets Made of Oklahoma Coal with Crude-Oil Residue as a Binder. J. C. Davis. *Coal Age*, Vol. 18 (1920), No. 9, pp. 443–444.

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Canadian Pulpwood Resources. D. M. Le Bourdais. *Paper*, Vol. 27 (1920), No 4, pp. 19, 42, 44.

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Coal-Saving in the Chemical Industry: The Scientific Control of Steam Boiler-Plant. David Brownlie. *The Chemical Trade Journal and Chemical Engineer*, Vol. 67 (1920), No. 1735, pp. 247–250; No. 1737, pp. 311–314; No. 1738, pp. 343–347.

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Distillation Plant, with Special Reference to the Rectification of Alcohol, Acetaldehyde, and Other Volatile Products, and Continuous Ether Manufacturing Plant. Stephane Masfaraud. *Journal of the Society of Chemical Industry*, Vol. 39 (1920), No. 17, pp. 299*t*–305*t*.

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MARKET REPORT—OCTOBER, 1920

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

	Oct. 1	Oct. 15
Acid, Boric, cryst., bbls............lb.	.17	.17
Hydrochloric, com'l, 22°.....lb.	.02¼	.02
Hydriodic..................oz.	.19	.19
Nitric, 42°..................lb.	.07¾	.07¾
Phosphoric, 50% tech.........lb.	.25	.25
Sulfuric, C. P..................lb.	.07	.07
Chamber, 66°...........ton	21.00	21.00
Oleum 20%.............ton	25.00	23.00
Alum, ammonia, lump............lb.	.04¾	.04¾
Aluminium Sulfate (iron-free)......lb.	.04½	.04½
Ammonium Carbonate, pwd.......lb.	.16	.16
Ammonium Chloride, gran........lb.	.14	.12½
Ammonia Water, carboys, 26°....lb.	.11	.11
Arsenic, white....................lb.	.14	.14
Barium Chloride................ton	120.00	120.00
Nitrate......................lb.	.14	.14
Barytes, white...................ton	30.00	30.00
Bleaching Powd., 35%, Works, 100 lbs.	6.75	6.75
Borax, cryst., bbls.................lb.	.09½	.09½
Bromine, tech....................lb.	.55	.55
Calcium Chloride, fused..........ton	33.50	33.50
Chalk, precipitated, light.........lb.	.05	.05
China Clay, imported............ton	18.00	18.00
Copper Sulfate..............100 lbs.	7.50	7.50
Feldspar.........................ton	8.00	8.00
Fuller's Earth...............100 lbs.	1.00	1.00
Iodine, resublimed.................lb.	4.35	4.35
Lead Acetate, white crystals.......lb.	.13	.13
Nitrate......................lb.	.15	.15
Red American..........100 lbs.	.12¼	.12¼
White American.........100 lbs.	.10½	.10½
Lime Acetate...............100 lbs.	3.50	3.50
Lithium Carbonate...............lb.	1.50	1.50
Magnesium Carbonate, Tech......lb.	.13	.13
Magnesite.........................ton	65.00	65.00
Mercury flask................75 lbs.	70.00	65.00
Phosphorus, yellow...............lb.	.35	.35
Plaster of Paris.............100 lbs.	1.50	1.50
Potassium Bichromate............lb.	.32	.31
Bromide, Cryst..............lb.	.50	.45
Carbonate, calc., 80–85%.....lb.	.20	.20
Chlorate, cryst...............lb.	.18	.18
Hydroxide, 88–92%..........lb.	.22	.22
Iodide, bulk..................lb.	3.25	3.25
Nitrate......................lb.	.14	.12
Permanganate, U. S. P........lb.	.70	.65
Salt Cake.........................ton	Nominal	Nominal
Silver Nitrate....................oz.	.59	.55
Soapstone, in bags...............ton	12.00	12.00
Soda Ash, 58%, bags........100 lbs.	2.65	2.50
Caustic, 76%...........100 lbs.	4.00	4.25
Sodium Acetate...................lb.	.12	.12
Bicarbonate............100 lbs.	3.00	3.00
Bichromate..................lb.	.17	.10½
Chlorate.....................lb.	.10	.10
Cyanide.....................lb.	.30	.30
Fluoride, technical...........lb.	.20	.20
Hyposulfite, bbls.......100 lbs.	4.00	4.00
Nitrate, 95%...........100 lbs.	3.50	3.00
Silicate, 40°.................lb.	.01½	.01½
Sulfide......................lb.	.08½	.08½
Bisulfite, powdered...........lb.	.07	.07
Strontium Nitrate...............lb.	.15	.15
Sulfur, flowers..............100 lbs.	3.75	4.00
Crude.................long ton	25.00	25.00
Talc, American, white...........ton	20.00	20.00
Tin Bichloride....................lb.	.21½	.21½
Oxide........................lb.	.60	.60
Zinc Chloride, U. S. P............lb.	.50	.50
Oxide, bbls..................lb.	.12	.12

ORGANIC CHEMICALS

	Oct. 1	Oct. 15
Acetanilide.......................lb.	.50	.45
Acid, Acetic, 28 p. c.........100 lbs.	3.75	3.75
Glacial..................lb	.12	.12
Acetylsalicylic...............lb.	.85	.85
Benzoic, U. S. P., ex-toluene..lb.	.80	.80
Carbolic, cryst., U. S. P., drs...lb.	.15	.15
50- to 110-lb. tins.........lb.	.23	.23
Citric, crystals, bbls..........lb.	.70	.65
Acid (*Concluded*)		
Oxalic, cryst., bbls............lb.	.38	.32
Pyrogallic, resublimed........lb.	2.35	2.35
Salicylic, bulk, U. S. P........lb.	.45	.40
Tartaric, crystals, U. S. P.....lb.	.65	.61
Trichloroacetic, U. S. P.... ..lb.	4.40	4.40
Acetone, drums..................lb.	.22	.22
Alcohol, denatured, 190 proof....gal.	1.13	1.13
Ethyl, 190 proof............gal.	6.00	5.50
Wood, Pure.................gal.	3.75	3.40
Amyl Acetate....................gal.	4.00	4.00
Camphor, Jap. refined...........lb.	1.20	1.20
Carbon Bisulfide..................lb.	.08	.08
Tetrachloride................lb.	.14½	.12
Chloroform, U. S. P..............lb.	.43	.43
Creosote, U. S. P.................lb.	.70	.70
Cresol, U. S. P....................lb.	.18	.18
Dextrin, corn......................lb.	.06¼	.06¼
Imported Potato............lb.	.11	.11
Ether, U. S. P., conc., 100 lbs......lb.	.24	.24
Formaldehyde....................lb.	.40	.27
Glycerol, dynamite, drums........lb.	.27	.25
Pyridine ....gal.	2.75	2.75
Starch, corn................100 lbs.	4.23	4.23
Potato, Jap..................lb.	.06½	.06½
Rice.........................lb	.25	.25
Sago.........................lb.	.05	.05

OILS, WAXES, ETC.

	Oct. 1	Oct. 15
Beeswax, pure, white.............lb.	.60	.60
Black Mineral Oil, 29 gravity.....gal.	.22	.22
Castor Oil, No. 3.................lb.	.14½	.14½
Ceresin, yellow...................lb.	.13	.13
Corn Oil, crude...................lb.	.08½	.08½
Cottonseed Oil, crude, f. o. b. mill..lb.	.09½	.07¾
Menhaden Oil, crude (southern)..gal.	.50	.50
Neat's-foot Oil, 20°..............gal.	1.65	1.65
Paraffin, 128–130 m. p., ref........lb.	.11½	.11½
Paraffin Oil, high viscosity......gal.	.45	.45
Rosin, "F" Grade, 280 lbs........bbl.	13.00	12.90
Rosin Oil, first run..............gal.	.72	.72
Shellac, T. N.....................lb.	.95	.90
Spermaceti, cake.................lb.	.30	.30
Sperm Oil, bleached winter, 38°...gal.	1.85	1.85
Stearic Acid, double-pressed.......lb.	.19½	.19½
Tallow Oil, acidless..............gal.	1.25	1.25
Tar Oil, distilled.................gal.	.60	.60
Turpentine, spirits of............gal.	1.38	1.27

METALS

	Oct. 1	Oct. 15
Aluminium, No. 1, ingots.........lb.	.32	.28
Antimony, ordinary..........100 lbs.	7.25	6.75
Bismuth..........................lb.	2.72	2.72
Copper, electrolytic..............lb.	.18¾	.16
Lake.......................lb.	.18¾	.16½
Lead, N. Y.......................lb.	.07¾	.07¼
Nickel, electrolytic...............lb	.45	.45
Platinum, refined, soft............oz.	110.00	110.00
Quicksilver, flask..........75 lbs ea	70.00	65.00
Silver...........................oz.	1.00	1.00
Tin..............................lb.	.43	.37½
Tungsten Wolframite........per unit	6.50	6.50
Zinc, N. Y..................100 lbs.	7.60	7.35

FERTILIZER MATERIALS

	Oct. 1	Oct. 15
Ammonium Sulfate..........100 lbs.	5.35	4.80
Blood, dried, f. o. b. N. Y........unit	8.00	8.00
Bone, 3 and 50, ground, raw......ton	48.00	48.00
Calcium Cyanamide, unit of Ammonia.........................	4.00	4.00
Fish Scrap, domestic, dried, f. o. b. works.......................unit	7.25	7.25
Phosphate Rock, f. o. b. mine:		
Florida Pebble, 68%........ton	6.85	6.85
Tennessee, 78–80%..........ton	11.00	11.00
Potassium Muriate, 80%........unit	2.25	1.75
Pyrites, furnace size, imported....unit	.18	.18
Tankage, high-grade, f. o. b. Chicago.......................unit	7.75	7.75

COAL-TAR CHEMICALS

		Oct. 1	Oct. 15
Crudes			
Anthracene, 80-85%	lb.	.75	75
Benzene, Pure	gal.	.35	.35
Cresol, U. S. P.	lb.	.18	.18
Cresylic, 97-99%	gal.	1.20	1.20
Naphthalene, flake	lb.	.13½	.10½
Phenol, drums	lb	.15	.15
Toluene, Pure	gal.	.35	.35
Xylene, 2 deg. dist. range	gal.	.60	.60
Intermediates			
Acids:			
Anthranilic	lb.	2.20	2.20
B	lb.	2 25	2.25
Benzoic	lb.	.80	.80
Broenner's	lb.	1.75	1.75
Cleve's	lb.	2.00	2.00
Gamma	lb.	4.25	4 00
H	lb.	1.80	1.70
Metanilic	lb	1.70	1.70
Monosulfonic F	lb.	3.50	3.50
Naphthionic, crude	lb.	.85	85
Nevile & Winther's	lb.	1.90	1.80
Phthalic	lb.	.60	.60
Picric	lb.	.25	.25
Sulfanilic	lb.	.33	.33
Tobias	lb.	2.25	2.25
Aminoazobenzene	lb.	1.15	1.15
Aniline Oil	lb.	.27½	.26
For Red	lb.	.65	.65
Aniline Salt	lb.	.33	.33
Anthraquinone	lb.	3.00	2.50
Benzaldehyde, tech	lb.	.65	.65
U. S. P.	lb.	1.00	1.00
Benzidine (Base)	lb.	1.25	1.15
Benzidine Sulfate	lb.	1.05	1.05
Diaminophenol	lb.	6.00	5.50
Dianisidine	lb.	9.00	8.00
p-Dichlorobenzene	lb.	.15	.15
Diethylaniline	lb.	1.55	1.50
Dimethylaniline	lb.	.90	.90
Dinitrobenzene	lb.	.36	.36
Dinitrotoluene	lb.	.43	.43
Diphenylamine	lb.	.80	.80
G Salt	lb.	.85	.80
Hydroquinone	lb.	2.20	2.00
Metol (Rhodol)	lb.	6.75	6.75
Monochlorobenzene	lb.	.15	.14
Monoethylaniline	lb.	2.15	2.15
α-Naphthylamine	lb.	.45	.45
β-Naphthylamine (Sublimed)	lb.	2.25	2.25
β-Naphthol, dist.	lb.	.68	.50
m-Nitroaniline	lb.	1.05	.90
p-Nitroaniline	lb.	1.25	1.15
Nitrobenzene, crude	lb.	.14	.14
Rectified (Oil Mirbane)	lb.	.16	.16
p-Nitrophenol	lb.	.80	.80
p-Nitrosodimethylaniline	lb.	2.90	2.90
o-Nitrotoluene	lb.	.25	.25
p-Nitrotoluene	lb.	1.50	1.50
m-Phenylenediamine	lb.	1.45	1.30
p-Phenylenediamine	lb.	2.30	2.30
Phthalic Anhydride	lb.	.65	.65
Primuline (Base)	lb.	3.00	3.00
R Salt	lb.	.90	.85
Resorcinol, tech	lb.	2.25	2.25
U. S. P.	lb.	2.75	2.75
Schaeffer Salt	lb.	.75	.75
Sodium Naphthionate	lb.	1.10	1.10
Thiocarbanilide	lb.	.60	.60
Tolidine (Base)	lb.	1.75	1.75
Toluidine, mixed	lb.	.44	.44
o-Toluidine	lb.	.33	.33
m-Toluylenediamine	lb.	1.50	1.50
p-Toluidine	lb.	1.75	1.75
Xylidine, crude	lb.	.50	.50

COAL-TAR COLORS

		Oct. 1	Oct. 15
Acid Colors			
Black	lb.	1.25	1.25
Blue	lb.	3.00	3.00
Acid Colors (*Concluded*)			
Fuchsin	lb.	2.50	2.50
Orange III	lb.	1.00	1.00
Red	lb.	1.30	1.30
Violet 10B	lb.	6.50	6.50
Alkali Blue, domestic	lb.	5.50	5.50
Imported	lb.	8.00	8.00
Azo Carmine	lb.	4.00	4.00
Azo Yellow	lb.	2.00	2.00
Erythrosin	lb.	12.00	12.00
Indigotin, conc	lb.	3.00	3.00
Paste	lb.	1.50	1.50
Naphthol Green	lb.	1.95	1.95
Ponceau	lb.	1.25	1.25
Scarlet 2R	lb.	1.00	1.00
Direct Colors			
Black	lb.	1.00	1.00
Blue 2B	lb.	.70	.70
Brown R	lb.	1.65	1.65
Fast Red	lb.	3.50	3.50
Yellow	lb.	2.00	2.00
Violet, conc	lb.	2.20	2.20
Chrysophenine, domestic	lb.	2.25	2.25
Imported	lb.	3.80	3.80
Congo Red, 4B Type	lb.	.90	.90
Primuline, domestic	lb.	3.00	3.00
Oil Colors			
Black	lb.	.70	.70
Blue	lb.	1.65	1.65
Orange	lb.	1.40	1.40
Red III	lb.	1.65	1.65
Scarlet	lb.	1.75	1.75
Yellow	lb.	1.70	1.70
Nigrosine Oil, soluble	lb.	.90	.90
Sulfur Colors			
Black	lb.	.20	.20
Blue, domestic	lb.	.70	.70
Brown	lb.	.35	.35
Green	lb.	1.00	1.00
Yellow	lb.	.90	.90
Chrome Colors			
Alizarin Blue, bright	lb.	7.75	7.75
Alizarin Red, 20% Paste	lb.	1.10	1.10
Alizarin Yellow G	lb.	1.00	1.00
Chrome Black, domestic	lb.	1.25	1.25
Imported	lb.	2.20	2.20
Chrome Blue	lb.	2.50	2.50
Chrome Green, domestic	lb.	2.00	2.00
Chrome Red	lb.	2.00	2.00
Gallocyanin	lb.	3.25	3.25
Basic Colors			
Auramine, O, domestic	lb.	2.50	2.50
Auramine, OO	lb.	4.15	4.15
Bismarck Brown Y	lb.	.90	.90
Bismarck Brown R	lb.	1.20	1.20
Chrysoidine R	lb.	.75	.75
Chrysoidine Y	lb.	.75	.75
Green Crystals, Brilliant	lb.	6.00	6.00
Indigo, 20 p. c. paste	lb.	.85	.85
Fuchsin Crystals, domestic	lb.	6.50	6.50
Imported	lb.	12.00	12.00
Magenta Acid, domestic	lb.	4.25	4.25
Malachite Green, crystals	lb.	4.50	4.50
Methylene Blue, tech	lb	2.75	2.75
Methyl Violet 3 B	lb.	3.00	3.50
Nigrosine, spts. sol	lb.	.85	.85
Water sol., blue	lb.	.70	.70
Jet	lb.	.90	.90
Phosphine G., domestic	lb.	7.00	7.00
Rhodamine B, extra conc	lb.	40.00	40.00
Victoria Blue, base, domestic	lb.	6.00	6.00
Victoria Green	lb	6.00	6.00
Victoria Red	lb.	7.00	7.00
Victoria Yellow	lb.	7.00	7.00

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CONTENTS

EDITORIALS:

President-Elect Harding's Views 1146
A Hurry Call 1146
Playing Their Game 1146
Machinery Installed—Lubrication Next 1147
Caught Up 1147
In the Game 1147
Notes 1148

ORIGINAL PAPERS:

Nature of the Hide-Tannin Compound and Its Bearing upon Tannin Analysis. John Arthur Wilson and Erwin J. Kern 1149
The Thermal Decomposition of Turpentine with Particular Reference to the Production of Toluene and Isoprene. S. A. Mahood 1152
The Aging of Certain Rubber Compounds. I. R. Ruby and Harlan A. Depew 1155
Some Microsections Cut from Vulcanized Rubber Articles. Harlan A. Depew and I. R. Ruby 1156
The Solubility of Metals in Acids Containing Formaldehyde. Roger C. Griffin 1159
The Acid Hydrolysis of Sugar-Cane Fiber and Cottonseed Hulls. E. C. Sherrard and G. W. Blanco 1160
Studies on Technical Casein. I—Introduction. W. Mansfield Clark 1162
Studies on Technical Casein. II—Grain-Curd Casein. W. Mansfield Clark, H. F. Zoller, A. O. Dahlberg and A. C. Weimar 1163
Studies on Technical Casein. III—Methods of Analysis. Roscoe H. Shaw 1168
Studies on Technical Casein. IV—Standardization of the Borax Solubility Test for Commercial Caseins. Harper F. Zoller 1171
Cellulose Acetates. J. O. Zdanowich 1173
The Direct Identification of Soy-Bean Oil. Charles A. Newhall 1174
The Oil of the Prickly Pear Seed. S. Lomanitz 1175
The Determination of Crude Fiber in Prepared Mustard. M. C. Albrech 1175
Orange Vinegar—Its Manufacture and Composition. Homer D. Poore 1176
Recent Advances in Defecation. W. D. Horne 1179
The Chemistry of Digitalis. Herbert C. Hamilton 1180
Hardness of Surface Waters of the United States. W. D. Collins 1181
The Determination of Acetic Acid in Pyroligneous Acid. V. E. Grotlisch 1183
The Determination of Hydrochloric Acid and Neutral Chlorides in Leather. Arthur W. Thomas and Alexander Frieden 1186
Some Results of the Determination of Potash by the Lindo-Gladding Method. H. C. Moore and R. D. Caldwell 1188
The Detection of Oils other than Linseed in Paints by Means of the Hexabromide Number of the Fatty Acids. Herbert Bailey and Walter D. Baldsiefen 1189
Naphthalene Sulfonic Acids. III—An Alternative Method for the Qualitative Detection of Naphthalene-2,7- and 1,6-Disulfonic Acids. Joseph A. Ambler 1194
The Influence of Potassium Permanganate on Kjeldahl Nitrogen Determinations. Donald C. Cochrane 1195
Note on the Catalysis of Permanganate Titrations. Paul H. Segnitz 1196

LABORATORY AND PLANT:

The Preservation of Bagasse in Sugar-Cane Mill Control. Guilford L. Spencer 1197
The Specific Heat of Petroleum at Different Temperatures. F. W. Bushong and L. L. Knight 1197
A New Illuminator for Microscopes. III. Alexander Silverman 1200
A New Conductivity Cell. Frank E. Rice 1202

ADDRESSES AND CONTRIBUTED ARTICLES:

American Progress in the Bacteriological Sugars. Edmund H. Eitel 1202
Unit Weights for the Purchase of Reagents. W. D. Collins 1206
A STUDY OF THE ECONOMIC STATUS OF CHEMISTS IN THE GOVERNMENT SERVICE, TEN EDUCATIONAL INSTITUTIONS AND THIRTY-SEVEN FIRMS. Lyman F. Kebler 1206

NOTES AND CORRESPONDENCE:

An Opportunity to Obtain the London Chemical Society's Annual Reports on the Progress of Chemistry at a Reduced Rate; Semi-Centennial Exercises at Ohio State University; News Items from the National Research Council; Department of Engineering Research at the University of Michigan; American Field Service Fellowships for French Universities; Washington University; Society of Mechanical Engineers; The Jelly Strength of Gelatins and Glues—Correction; Gasoline from Natural Gas. IV—Temperature Correction and Blending Charts—Correction; Relationship of Hydrogen-Ion Concentration of Natural Waters to Carbon Dioxide Content—Correction; Calendar of Meetings 1213
WASHINGTON LETTER 1215
LONDON LETTER 1216
PARIS LETTER 1217
INDUSTRIAL NOTES 1217
PERSONAL NOTES 1219
GOVERNMENT PUBLICATIONS 1220
BOOK REVIEWS 1223
NEW PUBLICATIONS 1227
MARKET REPORT 1228
AUTHOR INDEX 1230
SUBJECT INDEX 1235

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EDITORIALS

PRESIDENT-ELECT HARDING'S VIEWS

Frequently, since the recent election, we have heard the query "What is the attitude of the President-elect towards chemistry and the chemical industries?" Happily, we are in position to answer in the words of Senator Harding himself. An invitation to attend the Sixth National Exposition of Chemical Industries was sent to each member of Congress. The following acknowledgment was promptly received from Senator Harding:

Marion, Ohio,
Sept. 11, 1920

Mr. Charles H. Herty,
Chairman Advisory Committee,
National Exposition of Chemical Industries,
Grand Central Palace,
New York City, N. Y.

My Dear Mr. Herty:

I beg to acknowledge, with thanks, your letter of September 8th, inviting me to attend the Sixth Annual Exposition of Chemical Industries. If my engagements permitted I would be more than glad to accept for I am really tremendously interested in the work and progress that will be represented at the Exposition. The war taught us what we needed to make us truly a self-sustaining, independent nation and much will depend upon the success of our chemical engineers and producers to remedy the deficiencies which then became more impressibly apparent. May I ask you to convey to the members of your committee my thanks for the courtesy of the invitation and the regret of my inability to make acceptance.

With best wishes for your success, I am,

Sincerely yours,
(Signed) W. G. Harding

That is a fine sentence: *"The war taught us what we needed to make us truly a self-sustaining, independent nation and much will depend upon the success of our chemical engineers and producers to remedy the deficiencies which then became more impressibly apparent."*

A HURRY CALL

The following resolution and recommendation have been unanimously adopted by the American Chemical Society's Committee on National Policy (Advisory Committee):

(1) Be It Resolved, That the American Chemical Society, representing 15,500 chemists, affirms its great interest in the United States Patent Office, and believes that it is vitally essential to the welfare and progress of the industries of the United States. Representatives of the Society have endorsed most heartily the Nolan Patent Office Bill, H. R. 11,984, as passed by the House of Representatives last spring. We are very deeply concerned at the reduction in the examining and clerical forces and in the salaries provided, which was made by the United States Senate in passing this bill. The numbers and salaries proposed in the original bill, we believe, are as low as they can possibly be made, and still relieve effectively the present desperate situation in the Patent Office. The American Chemical Society accordingly urges most strongly that the numbers of the examining and clerical force for the Patent Office, and the salaries provided in the bill as passed by the House of Representatives should be restored. The Society also recommends that the bill should be freed from riders, such as Section 9 thereof, in the Senate bill, which might delay or jeopardize the passage of the bill. We also urge that the bill should be made a law at the earliest possible moment.

(2) The American Chemical Society having, on the 15th day of November 1920, passed a resolution urging the restoration to their original values of the numbers for the examining and clerical forces of the Patent Office and the salaries therefor in the Nolan Patent Office Bill, H. R. 11,984, and that the bill should be freed from riders, such as Section 9 thereof, in the Senate bill, which might delay or jeopardize the passage of the bill, urgently recommends that members of the Society communicate with their representatives and senators in Congress urging action in accordance with the said resolution.

The rider referred to was attached to the bill by the Senate Committee on Patents, giving power to the Federal Trade Commission to receive assignments of patents and to grant licenses thereunder. There is a difference of opinion among chemists as to the wisdom of granting to the Federal Trade Commission the authority to receive assignments of patents, and to grant licenses thereunder. There is no difference of opinion about granting to the Patent Office that full measure of relief contemplated in the original measure. Let each tub stand on its own bottom and let the Patent Office be enabled to measure up to that full possibility of its usefulness which can so deeply serve the interests of our people.

The bill has been sent to a Conference Committee, the members of which include Senators Geo. W. Norris, of Nebraska, Frank B. Brandegee, of Connecticut, and William F. Kirby, of Arkansas. The members from the House have not yet been appointed, but following custom, Representative John I. Nolan, Chairman of the House Committee on Patents, will undoubtedly be a member. Write to them!

The request of the Committee on National Policy is made of each member of the Society individually. Each resident member of the Society has a representative in Congress. Let him know your views. Do it to-day!

PLAYING THEIR GAME

Two interesting pieces of printed matter were received in our mail on the morning of November 17, 1920. The first was the November Bulletin of the American Electrochemical Society, issued over the official signature of Jos. W. Richards, Secretary. Among the items in this Bulletin was one giving the status in Congress of House Bill 7785 (the Bacharach bill), one feature of which is the repeal of Section 573 of the Tariff Act of 1913 giving to educational institutions the privilege of importing scientific instruments, etc., duty-free. All interested in our educational institutions were urged by the Secretary to write to the Chairman of the Senate Finance Committee and request the elimination of this feature of the bill.

The second bit of interesting material was a pink sheet, printed fore and aft, which a Harvard correspondent forwarded us. This sheet covered the same ground as that covered by Professor Richards' remarkable exhortation, only at much greater length and shot through with sentences which plainly suggested Teutonic English. We looked for the signature and found to our surprise merely: **Friends of Science, interested in its development.** That sounded like the early days of war-time when the "Friends of Peace" were so active with their treacherous propaganda.

We studied the two articles more closely and also comparatively. Here is the result:

Secretary Richards' Exhortation	"Friends of Science" Propaganda
"recommended for passage without amendment by the Committee of Finance of the United States Senate. (Report 4459)."	"recommended for passage without amendment by the Committee of Finance, United States Senate. (Report 459)."
"repeals section 573 of the tariff act of October 3, 1913, for duty-free importation of scientific instruments and scientific glassware by educational institutions."	"repeals section 573 of the tariff act of October 3, 1913, for the duty-free importation by educational institutions."
"This bill will soon be presented for final action in the United States Senate."	"This bill will soon be presented for final action in the United States Senate."

Each urges that readers write to the "Chairman of the Senate Committee of Finance, Senate Office Building, Washington, D. C." Even the erroneous "of" for "on" is duplicated by the Secretary and by the "Friends of Science, interested in its development."

We got busy. A telephone call to our correspondent at Harvard elicited the information that the pink slips were being distributed by a representative of E. Leitz, Inc., of New York City, importers of German scientific instruments. An unknown representative of This Journal called at the salesrooms of E. Leitz, Inc., and after some cautious questioning received direct from their representative another copy of the pink slip. Later by telephone this same representative received from some one at E. Leitz's an admission that they were responsible for the writing and printing of the circulars.

Evidently, from the comparison of the two pieces of printed matter, the Secretary of the American Electrochemical Society had fallen for the bait and was playing their game. No one can question his right as an individual to fight the Bacharach bill, however much all interested in the continuance of our American industries might regret it; but that this plea should be put out in an official document over his signature as Secretary was amazing, for we did not believe the Electrochemical Society had taken such action or would endorse any such request. We immediately wired the Secretary asking if the statement represented official action of the American Electrochemical Society. We also wrote Dr. W. S. Landis, President of the Society, asking the same question. On Monday, November 22, the Secretary, who we understand had been absent in Washington, replied "Statement not official Society action." On the same day President Landis wrote us as follows:

> "This matter has not received attention from either the Board of Directors of the American Electrochemical Society or at any of the general meetings of the Society. I am, therefore, desirous of correcting any erroneous impression that might become current that the American Electrochemical Society has officially taken such stand on this Bill as is indicated in the Bulletin. In fact the majority of the Board of Directors are opposed to such elimination as has been urged by the Secretary of the Society."

The question of secretarial prerogatives is one which lies between the Directors of the American Electrochemical Society and the Secretary.

The incident represents the kind of stuff American manufacturers who have capably filled the country's need in a critical period have to contend with while the Senate waits on Senator Penrose to give the word.

MACHINERY INSTALLED—LUBRICATION NEXT

A great gathering of Anglo-Saxon chemists in New York City is assured. The editorial suggestion in our July issue made its appeal to all and the machinery has now been installed with which to carry out this important process of "rope-making."

The British Society of Chemical Industry has accepted the invitation to meet with its Canadian Sections during the last week of August 1921, in Montreal. Following an extensive excursion, the last stage of which will lead to New York City, the travelers will be welcomed by the American Section of the Society of Chemical Industry and by the American Chemical Society, which is to hold its Annual Meeting in the same city from September 7 to 10, 1921. The Seventh National Exposition of Chemical Industries has been advanced to the week of September 12 to 17, 1921.

The next step is thorough lubrication. We mean the appointment of efficient and energetic coöperative committees which will plan wisely for the smooth functioning of so potent a joint assemblage. It may be counted upon as a certainty that this work, already begun, will be well done.

It is hoped sincerely that between now and the time for the actual rope-making to begin our respective governments will provide adequate plant housing in the form of protective legislation. There are those who will leave no stone unturned to prevent this, but sabotage must not be allowed. Too much is at stake.

CAUGHT UP

We are happily in position to announce that we have now "caught up" in the publication of original papers. This is the result of the thorough work of the reviewers and the fine-spirited acceptance by authors of recommendations for condensation and elimination of inessentials. There is now no reason for delay other than is consistent with careful review, provided, of course, that papers are concisely written and free from unnecessary details.

IN THE GAME

In this editorial work which has fallen to our lot, we have to browse about a good deal. In the course of these browsings many things of interest turn up. The constantly increasing total of capital invested in the chemical industries, the logical combinations of allied chemical organizations, the continuous growth of industrial research—these are easily apparent and give rise to feelings of confidence as to the future security of our industry. But that which fascinates us most is the growing number of small groups and particularly of individuals who, guided by the one thought of making America economically independent, and somewhat in the spirit of entering a sport, have selected certain needed individual products, and by applying the methods of research combined with the American spirit of daring and ingenuity, are doing real stunts in developing these products in quality better than ever known.

Recently we lunched with a chemist who has set himself the problem of giving to American artists the best pigments ever used, so that no need shall exist for looking abroad for artists' colors, and he is turning the trick.

In the recent filter paper discussion we could not shake off the regret that there was no American product which could take precedence over all others. We turned naturally to Dr. A. D. Little to urge him to get into this game in earnest. He replied:

> We have been sticking hard to the problem of producing the best filter paper in the world and have already spent about $..,... on experimental runs. * * * * As a result of our last ten runs, we now have in stock paper enough for something over 3,000 boxes of the 11 cm. size. We have now reached the point where we are confronted with an expenditure of $..,... to $..,... more to put our experimental paper mill on a commercial basis and as we are in the game to stay, I think there is no doubt that our Executive Committee will authorize this expenditure. When we put the paper out we propose to stand by it as the very best that can be made.

It is easy to understand Dr. Little's confidence, for we have seen the results of official tests of this paper, which unfortunately we are not free to publish, but the Director of the U. S. Bureau of Standards has given us permission to publish the following letter:

> DEPARTMENT OF COMMERCE
> BUREAU OF STANDARDS
> WASHINGTON
>
> October 19, 1920
>
> Subject: Filter Paper
>
> ARTHUR D. LITTLE, INC.,
> Cambridge, Massachusetts.
>
> GENTLEMEN:
>
> Referring to our letter of September 16, 1919, giving our report on filter paper manufactured by your company, we would thank you to advise whether this paper has been put on the market. This paper showed up so well in our tests that *we hailed it as an American product that would render the chemists of this country independent of all foreign sources.* [Italics ours.] If this paper were put on the market and advertised, it is believed that the undertaking would receive the united support of the chemists of America. We shall be pleased to have your views on the matter. Please address your reply to the attention of Section 5, Division V.
>
> Respectfully,
> (Signed) S. W. STRATTON, *Director*

Plainly the day is not far distant when the forging of this link in our industrial chain will be completed. On with the game! It's a fine sport!

Again these browsings sometimes develop very funny things. Here is one which has just come to us. We know it is authentic but will not publish names. A certain New England mill employing a certain German dyer has long used a certain dye. When German importations ceased a certain American firm went into this game, made the dye and supplied the mill. But when German colors again became restrictedly available, the German dyer insisted he must have his "good old German dye." The mill superintendent, with too often characteristic lack of backbone, was afraid to make the issue, so the shipment of the American product was stopped. A little later the supposedly "good old German dye" turned up at the mill, and since that time the old German dyer has been content. As a matter of fact, he is to-day using the same American dye he used during the war, only it is reaching him through a rather unscrupulous broker who is delivering the American product under German trappings and receiving from the consumer a comfortable commission for his part in the little game of fraud.

NOTES

The Rochester Section has already started out to make the 1921 Spring Meeting of the Society an even greater success than the memorable meeting of 1913.

If there be any who still question the wisdom of the Council in raising the annual dues 50 per cent, it may be of interest to learn that the Chemical Society (London) has increased its dues from 2 to 3 pounds, the Society of Chemical Industry from 30 to 50 shillings, and the American Pharmaceutical Association from $5.00 to $7.50, annually.

The War Trade Board is endeavoring to carry out in fairness to all its policy of granting license to import only such dyes as are not available from domestic sources in adequate quantity, of good quality and at a reasonable price. The successful carrying out of this policy can be accomplished only by the whole-hearted coöperation of our dye manufacturers in furnishing the Board full and accurate information as to products now being manufactured.

There will be universal regret over the announcement of the retirement of Dr. William H. Walker from the staff of the Massachusetts Institute of Technology. Twenty-five years of service as intensive as Dr. Walker has given to his work would be a serious drain upon the vitality of any man, but to this must be added the terrific strain of the war period during which Dr. Walker rendered signal service to his country, first in the development of the Chemical Warfare Section of the National Army, and later in that soul-racking undertaking of pushing to completion the great plant for the production of toxic gases at Edgewood Arsenal. Dr. Walker intends to carry on consultation work and will, of course, coöperate in the development of the Institute's Division of Industrial Coöperation and Research. His successor in this Division is Professor Charles L. Norton.

While Professor Soddy (Oxford) was declining his government's request to share in chemical warfare activities, and while the group of Oxford professors were laying themselves open to the unrepentant forgiveness of their German brother-servants, we noticed these bits of news in foreign dispatches. According to a Geneva cable to the *New York Sun* of November 22, the report of the League of Nations' permanent advisory commission on military, naval and air questions will say:

> It is useless to seek to restrict the use of gases in war time by prohibiting manufacture in peace time. It is impossible to prohibit laboratory experiments. The use of poison gas is fundamentally cruel, but no more than other methods if it is used against combatants only.

According to the *New York Times* "They [the Bolsheviki] owe their success largely to the use of poison gas." The *New York Globe* of the same date says: "It is reported that General Budenny's cavalry is commanded by German officers, that it is well equipped, and that it uses gas in its attacks." We had not thought of disorganized Russia as the home of a strong chemical industry. Had you?

ORIGINAL PAPERS

NATURE OF THE HIDE-TANNIN COMPOUND AND ITS BEARING UPON TANNIN ANALYSIS[1]

By John Arthur Wilson and Erwin J. Kern

Laboratories of A. F. Gallun & Sons Co., Milwaukee, Wisconsin

Received September 2, 1920

In an earlier paper[2] the authors described a new method of tannin analysis which they believe gives the true tanning value of vegetable materials. Comparative tests showed the official method of the American Leather Chemists' Association to be greatly in error, exceeding 200 per cent for typical samples of gambier extract. (The earlier paper should be referred to for a working description of both methods.) The much higher percentages of tannin obtained by the A. L. C. A. method for every material examined were attributed to the formation of readily hydrolyzable compounds between the hide powder and a variable fraction of the non-tannins. At the 17th annual meeting[3] of the A. L. C. A. a formal discussion[4] of this paper was staged, and the chief aim of the opposition was apparently to show that the low results obtained by the new method were due to losses of tannin in the manipulation. It was contended that a certain proportion of the tannin of a liquor will form a stable compound with hide only after long contact, and, further, that even tannin which has already combined with the hide will be removed to an appreciable extent during the washing required by the new method; but no really conclusive evidence was offered in support of these contentions. The object of the present work was to investigate these points because they are of great importance, not only to the new method, but to the theory and practice of tanning itself.

TANNING MATERIALS EXAMINED

Certain differences in behavior of the several different tanning materials have caused a widespread belief that some tannins form more stable compounds with hide than others; for example, the tannin from gambier is supposed to form a compound with hide less stable than that from hemlock bark. It has also been supposed that mixtures of tanning materials behave differently in this respect from the individual materials. We have therefore chosen for examination typical commercial tanning extracts ranging in properties from the extremes of gambier and sumac to those of hemlock and quebracho, and have also included two mixtures, each consisting of a pair of extracts of very different nature. The analyses of the 8 extracts and 2 mixtures, both by the new method and by the official method of the American Leather Chemists' Association, are given in Table I, along with the percentage errors involved in the A. L. C. A. method, assuming that the new method is correct.

TABLE I—COMPARATIVE ANALYSES OF EXTRACTS STUDIED, BY NEW METHOD AND BY THE A. L. C. A. METHOD

	Percentage Analysis of Material					Per-
	A. L. C. A. Method					centage
			Soluble Matter		New	Error in
Extract	Water	Insoluble Matter	Non-tannin	Tannin	Method Tannin	A.L.C.A. Method
Quebracho	22.28	9.61	7.24	60.87	46.84	30
Gambier	50.17	7.43	16.79	25.61	7.87	225
Quebracho-gambier mixture	44.53	7.39	14.86	33.22	20.67	61
Oak bark	52.43	3.10	18.28	26.19	15.52	69
Chestnut wood	52.47	3.64	18.19	25.70	13.99	84
Hemlock bark	56.10	6.23	10.99	26.68	23.47	14
Chestnut wood-hemlock bark mixture	53.89	5.94	14.53	25.64	18.73	37
Larch bark	51.26	7.42	18.36	22.96	11.29	103
Sumac	51.24	1.01	22.24	25.51	16.36	56
Wattle bark	50.20	1.50	14.75	33.55	24.66	36

It is interesting to compare the errors found for the sumac and hemlock bark extracts with those for the actual leaves and bark noted in the earlier paper. Extract manufacturers often remove only about 80 per cent of the tannin from the raw materials, because in order to get the last 20 per cent they would have to extract a large proportion of undesirable non-tannins that would considerably lower the purity of their products. The raw materials used were extracted completely and therefore contained a higher ratio of non-tannin to tannin than the commercial extract, and this, as the authors have shown, increases the error obtained by the A. L. C. A. method.

RESISTANCE OF LEATHER TO WASHING

Three methods of measuring possible losses of combined tannin during the washing of leather were considered. The first was to wash the leather free from soluble matter and analyze it for tannin, and then to wash it further and analyze it again. The second was to use the gelatin-salt reagent (10 g. gelatin plus 100 g. NaCl per liter) in testing the wash waters for tannin; provided all tests were negative, it would show that only a very small amount of tannin, if any, was washed out. The third was to collect and weigh the soluble residues from a number of wash waters. Of these, the first method appeared most important and consequently received greatest attention.

TABLE II—SHOWING EFFECT OF EXCESSIVE WASHING OF THE TANNED HIDE POWDER UPON THE PER CENT OF TANNIN FOUND BY THE NEW METHOD

			Per Cent Tannin in Extract. Value Obtained from Analysis of		
			Tanned Powder Washed		
Extract	Extract Grams in 200 Cc. Soln.	Hide Substance in Powder Used to Detannize 200 Cc. Soln. Grams	15 Times	25 Times	50 Times
Quebracho	3.80	10.44	46.84	47.25	46.90
Gambier	10.00	10.44	7.87	7.89	7.67
Quebracho-gambier mixture[1]	6.90	10.44	20.67	20.34	20.43
Oak bark	13.60	10.40	15.52	15.36	15.35
Chestnut wood	13.60	10.32	.....[3]	13.99	13.93
Hemlock bark	13.00	10.32	23.47	23.38	23.50
Chestnut wood-hemlock bark mixture[2]	13.30	10.32	.....[3]	18.73	19.05
Larch bark	13.60	10.32	.....[3]	11.29	11.28
Sumac	13.00	10.39	16.36	16.29	16.39
Wattle bark	8.00	10.32	24.66	24.16	24.73

[1] Mixture of 19 parts solid quebracho extract to 50 of gambier extract.

[2] Mixture of 68 parts of chestnut wood extract to 65 of hemlock bark extract.

[3] Calculation not made because 15th wash water gave test for non-tannin with ferric chloride.

PROCEDURE AND RESULTS—Portions of all 10 samples were dissolved in water to give the concentrations noted in Table II. For each sample 12 g. of air-dry hide powder, of known hide-substance content, were put into each of five wide-mouth, half-pint bottles, 200 cc. of tan liquor were added to each, and the bottles stoppered and shaken in a rotating box for 6 hrs. At the end of this time all solutions gave a negative test for tannin with the gelatin-salt reagent. The bulk of detannized liquor was removed from each powder by squeezing through a suitable cloth. Two powders from each set were allowed to dry slowly, without previous washing, and bottled for use in connection with an investigation of the "aging" of leather to be mentioned later. The remaining three powders of each set were washed as follows: Each powder was returned to its bottle along with 200 cc. water and shaken for an hour. The aqueous extract was separated from the powder by squeezing through a cloth, and the washing operation was repeated. Of the three powders of each set, one was washed fifteen times, the second twenty-five times, and the third fifty times. After washing, the tanned powders were allowed to dry slowly, and were then analyzed for water, ash, fat (chloroform extract), and hide substance (nitrogen × 5.62). The per cent of tannin was calculated by difference. The results are given in Table II.

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[1] Presented before the Section of Leather Chemistry at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

[2] "The True Tanning Value of Vegetable Tanning Materials," This Journal, **12** (1920), 465.

[3] Atlantic City, N. J., May 27 to 29, 1920.

[4] Printed in full, *J. Am. Leather Chem. Assoc.*, **15** (1920), 451.

The detannized liquor and fifteen wash waters from one of the gambier samples were evaporated separately to show the rate at which the soluble matter is removed by washing. Table III shows that only 12 mg. of soluble matter were removed by the fifteenth wash water, which appeared colorless and gave no color upon addition of a drop of ferric chloride solution. The smallness of the weights of the residues made the evaporation of individual wash waters beyond the fifteenth of doubtful value. However, all wash waters from the twenty-sixth to the fiftieth (5000 cc. in all) were collected from both the sumac-tanned and larch-tanned powders, and evaporated to dryness. The total matter extracted from the former was only 67 mg., and from the latter only 51 mg. Pure hide powder washed in the same way was found to yield even greater residues because of slow hydrolysis, and it should be remembered that hide powder was used in great excess in these tests. If the 67-mg. residues from the sumac-tanned powder consisted solely of hide substance, it would contain 12 mg. of nitrogen; a Kjeldahl determination gave 14 mg. Furthermore, the residues from the tanned powders resembled those from pure hide substance in odor and general appearance.

TABLE III—SHOWING SPEED OF WASHING OF POWDERS TANNED WITH GAMBIER

SOLUBLE RESIDUE FROM	Weight Mg.
Original detannized solution	1408
1st wash water	776
2nd wash water	396
3rd wash water	250
4th wash water	160
5th wash water	101
6th wash water	68
7th wash water	45
8th wash water	33
9th wash water	31
10th wash water	22
11th wash water	17
12th wash water	16
13th wash water	13
14th wash water	12
15th wash water	12

All wash waters without exception gave negative tests with the gelatin-salt reagent. Baldracco and Camilla[1] recently proposed a reagent for which they claimed greater sensitivity than the gelatin-salt reagent. Their reagent was made by dissolving 0.9 g. gelatin in 50 cc. water and adding 10 cc. of glacial acetic acid. While this solution appears to be more sensitive than a gelatin-salt solution which has been kept for some weeks, we found it much less sensitive than the gelatin-salt reagent immediately after preparation. When the gambier liquor was diluted 100 times and a drop of freshly prepared gelatin-salt reagent was added, a distinct precipitate was formed, whereas a freshly prepared gelatin-acetic acid reagent gave a negative test. We found that the gelatin-salt reagent must be prepared from the highest quality gelatin and used only on the day it was made for the most satisfactory results. The gambier liquor had to be diluted 200 times before it failed to give a test, and all the other liquors even more. Since no tests were obtained for any wash waters, at the end of fifteen washings not more than 8 per cent of the tannin originally present in the tan liquor could have been removed by washing. In other words, even if, as is most unlikely, each wash water removed an amount of tannin that would just fail to give a test with the gelatin-salt reagent, we should have to increase the per cent of tannin found for gambier extract, the material least sensitive to the test, only from 7.87 to 8.55, whereas a figure of 25.61 is obtained by the A. L. C. A. method.

CONCLUSIONS—The results show conclusively that prolonged washing is quite without influence upon the values obtained for the per cent of tannin in various materials by the new method, and, further, that tannin once combined with hide cannot be washed out by any amount of washing that would be practical. Thus the major contention of opponents of the new method is disproved.

ANOTHER VALUABLE PROPERTY OF CERTAIN NON-TANNINS NOT BEFORE FULLY RECOGNIZED

In our earlier paper it was shown that non-tannins like gallic acid are valuable agents in rendering too astringent tan liquors sufficiently mild for practical use. We now find that these same non-tannins are capable of undergoing chemical change with the formation of substances capable of tanning. During his criticism of the new method, G. W. Schultz[2] said, "We have taken the non-tannins and washings and reconcentrated them under a high vacuum to the original volume of 200 cc. and have tanned hide powder with it, and, by the calculations employed, we have found a definite percentage of tannin." He mentioned also that the concentrated liquor gave a positive test for tannin with the gelatin-salt reagent. It might look at first sight as though the detannized liquor and wash waters, before concentrating, really had contained tannin and Schultz evidently so regarded it. This view, however, would be difficult to reconcile with the experimental data noted in the preceding section.

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[1] *J. Soc. Leather Trades' Chem.*, **4** (1920), 101.

[2] *J. Am. Leather Chem. Assoc.*, **15** (1920), 455.

We confirmed Schultz's findings while analyzing a sample of gambier extract by the new method. The detannized liquor and 15 wash waters, all of which gave no test with the gelatin-salt reagent, were concentrated to 200 cc., whereupon they were found to give a bulky precipitate with the reagent. *But, when diluted back to 3200 cc., they still gave a bulky precipitate with the gelatin-salt reagent, showing that a most important chemical change had taken place during the concentrating.*

TABLE IV—GAMBIER EXTRACT

200 cc. solution containing 9.00 g. extract were detannized with 12 g. air-dry hide powder, containing 10.40 g. hide substance, and then the tanned powder was washed 17 times with 3400 cc. water. The residual liquor and wash waters were evaporated to 250 cc. and used to tan 12 g. fresh hide powder, which was afterwards washed as usual.

Total tannin either originally present or formed during the concentrating of the wash waters, 13.50 per cent.

	HIDE POWDER TANNED IN	
ANALYSIS OF AIR-DRY LEATHER	Original Solution	Concentrated Wash Waters
Water	17.31	16.24
Ash	0.16	0.14
Fat	0.39	0.42
Hide substance (N × 5.62)	76.86	79.38
Tannin (by difference)	5.28	3.82
Per 100 g. hide substance:		
Tannin found, grams	6.87	4.81
Material used, grams	86.54	86.54
Per cent tannin in extract	7.94	5.56

Another sample of gambier was analyzed by the new method and found to contain 7.94 per cent tannin. The detannized liquor and 17 wash waters (3600 cc. in all) were evaporated to 250 cc., analyzed by the new method, and found to contain 5.56 parts of tannin per 100 of original extract, giving the extract a total of 13.50 per cent tannin. The detailed results are given in Table IV. In order to show that this increased amount of tannin would have combined with the hide powder had it been present in the original solution, we made up a new solution of this extract, concentrated and diluted back several times, and then analyzed it by the new method, finding 12.69 per cent of tannin. If the concentrating had been continued a little longer the figure 13.50 would probably have been reached or passed. The results are given in Table V.

TABLE V—GAMBIER EXTRACT

(Same as noted in preceding table.)

Dissolved 60.00 g. extract in 1 liter of water. Concentrated to 250 cc., and diluted back to 1 liter. Repeated 3 times, the fourth time diluting to 2 liters. 200 cc. diluted solution containing 6.00 g. original extract were detannized with 12 g. air-dry hide powder, containing 10.37 g. hide substance, which was afterwards washed as usual.

ANALYSIS OF AIR-DRY LEATHER	
Water	18.23
Ash	0.18
Fat	0.42
Hide substance (N × 5.62)	75.62
Tannin (by difference)	5.55
Per 100 g. hide substance:	
Tannin found, grams	7.34
Material used, grams	57.86
Per cent tannin in extract	12.69

In spite of the great change in the tan liquor produced by concentrating, it is not shown to any appreciable extent in the analyses by the A. L. C. A. method shown in Table VI. Concentrating the tan liquor and diluting back caused a rise in per cent of tannin by the new method from 7.94 to 12.69, but the rise in the A. L. C. A. method is only from 26.14 to 26.40, which difference is so small as even to be attributable to experimental error. The reason for this small difference is probably that the non-tannins which are convertible into tannin all combine with the hide initially, even though they are easily removed later by washing.

TABLE VI—GAMBIER EXTRACT

Both the original liquor noted in Table IV and the specially treated liquor noted in Table V were appropriately diluted and analyzed by the A. L. C. A. method.

	PER CENT OF ORIGINAL EXTRACT	
	Original Liquor	Treated Liquor
Insoluble matter	7.66	8.62
Non-tannin	18.33	17.57
Tannin	26.14	26.40

Just what chemical actions are involved in the conversion of non-tannin to tannin must remain a matter of speculation until more data are available; oxidation, condensation, and polymerization may all be involved. It is conceivable that gallic acid might be converted into digallic acid under suitable conditions, and it seems extremely likely that a polymerized form of digallic acid would have tanning properties. A solution of pure gallic acid gives no test for tannin, but after boiling for some time it gives a bulky precipitate with the gelatin-salt reagent, and apparently will tan hide. A detannized solution which gives no test for tannin can be made to give a strong test merely by passing oxygen gas through it. Long exposure to air has a similar action. It is evident that the new method furnishes a valuable means of studying the conversion of non-tannins into tannin, and might conceivably be applied to a study of the formation of tannins in nature and to the aging of barks.

THE TIME FACTOR IN TANNING AND THE "AGING" OF LEATHER

The results of the preceding section suggest that the conversion of non-tannin into tannin is responsible for two factors of great importance to tanners of heavy leather, namely, the time factor in tanning and the "aging" of leather. In the discussion referred to, Alsop[1] remarked that sole leather tanned slowly not only contains more tannin, but actually consumes less tanning material than the rapid tannages. In a private communication, Professor Procter, of Leeds, has called attention to the fact that leather stored for a long time, or "aged," before washing contains more tannin than if it had been washed immediately after tanning. The extent of this aging is well shown in the following experiment:

TABLE VII—EFFECT OF "AGING" UPON PER CENT OF COMBINED TANNIN IN LEATHER

Two 12-g. portions of hide powder were used to detannize 200-cc. portions of the solutions of tanning materials noted in Table II. One portion in each case was washed 25 times immediately after tanning; the other portion was allowed to dry without washing, kept exactly 30 days, and then washed 25 times.

	TANNIN AS PER CENT OF ORIGINAL EXTRACT	
EXTRACT	In Leather Washed Immediately after Tanning	In Leather Kept 30 Days before Washing
Quebracho	47.25	53.00
Gambier	7.89	10.49
Quebracho-gambier mixture	20.34	23.92
Oak bark	15.36	17.23
Chestnut wood	13.99	18.02
Hemlock bark	23.38	24.87
Chestnut wood-hemlock bark mixture	18.73	20.45
Larch bark	11.29	13.22
Sumac	16.29	17.94
Wattle bark	24.16	25.89

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[1] *Loc. cit.*, p. 464.

In the work on the resistance of leather to washing, we tanned five portions of hide powder with each sample of tanning material examined, of which three were washed immediately after tanning and two dried without washing. After thirty days the washing of one of these powders from each set was begun. After the twenty-fifth washing it was dried and analyzed for comparison with the powders washed immediately after tanning. The results in Table VII show a distinct increase in tannin due to aging. It is intended to keep the fifth powder of each set for a full year before washing.

SUITABILITY OF THE NEW METHOD AS A STANDARD

We believe that the experimental data in this and the earlier paper prove not only that the new method is correct, but that the A. L. C. A. method, and, therefore, also the official methods of Europe, are greatly in error. In actual practice we found barely 50 per cent as much tannin in the leather coming from a certain upper leather yard during a 3-yr. period as was put into it, according to the analysis by the A. L. C. A. method of the extracts used. On the other hand, the new method now checks this yard easily within the limits of experimental error. We feel justified in recommending that the new method, or some modification of it, be adopted as a standard to replace the present official methods.

It has been contended, and perhaps rightly, that the new method is so time-consuming as to make it unpopular for routine work, but it should be realized that no serious effort has yet been made to simplify the method, all work up to the present having been confined almost exclusively to the question of correctness. One modification that appears promising for routine control work is to tan the hide powder as usual, transfer it to an alundum thimble, wash it by means of a mechanical arrangement, and then dry and weigh it, the increase in weight of the dry hide powder being taken as tannin. No doubt other modifications will suggest themselves as the work proceeds, but the saving of time is not sufficient compensation for the errors involved in the official methods.

SUMMARY

Tannin once combined with hide cannot be removed to an appreciable extent by any amount of washing that would be practical.

It has been discovered that chemical changes are produced in a tan liquor by boiling or evaporating, whereby certain non-tannins are converted into substances capable of tanning. Such changes can be followed quantitatively by means of the authors' new method for tannin analysis, but not by the official method of the American Leather Chemists' Association. The new method can also be used to study the "aging" of leather.

The new method gives results which agree closely with tanning practice, whereas the A. L. C. A. method was found to be greatly in error.

It is recommended that the new method be adopted as a standard.

THE THERMAL DECOMPOSITION OF TURPENTINE WITH PARTICULAR REFERENCE TO THE PRODUCTION OF TOLUENE AND ISOPRENE

By S. A. Mahood

FOREST PRODUCTS LABORATORY, MADISON, WISCONSIN

Received August 21, 1920

The decomposition of turpentine by heat was first investigated by Berthelot[1] and later by Hlasiwetz,[2] Schultz,[3] and Tilden.[4] Hlasiwetz passed turpentine vapors through a red-hot iron tube filled with porcelain, and obtained a liquid which had the odor of benzene, and from which was obtained on distillation a fraction which began to boil at 30°. Schultz, using an iron tube heated to dull redness, obtained a liquid which contained benzene, toluene, xylene, unchanged turpentine, naphthalene, phenanthrene, anthracene, and methylanthracene. Large quantities of combustible gas were also formed during the heating.

Tilden showed the low boiling product obtained by Hlasiwetz to be identical with isoprene obtained by Williams[5] by the distillation of India rubber. He also showed that the difference between the results obtained by Hlasiwetz and Schultz was due to a difference in the temperature of the tube through which the vapors were passed.

The discovery by Tilden[6] that isoprene polymerizes to India rubber has led to considerable experimental work on the production of isoprene from the terpenes. Aside from the patent literature, however, the yields reported have in the main been too low for practical purposes. Harries[7] obtained 1 per cent of isoprene from commercial pinene, using his isoprene lamp. Herty and Graham[8] obtained 5.5 per cent (by volume) of isoprene from turpentine, and 8 per cent from a fraction boiling between 155° and 156°. Using commercial limonene, Harries obtained a yield of 30 to 50 per cent of isoprene, while Herty and Graham obtained 12 per cent from a limonene fraction. Staudinger and Klever[9] obtained a yield of 60 per cent of isoprene from limonene by working at a pressure of 4 mm.

According to patents issued to Schering and Company,[10] larger yields of isoprene are obtained from β-pinene than from α-pinene, but Schorger and Sayre[11] found that these two terpenes give approximately the same amount of isoprene when passed through the same apparatus for purposes of comparison, the yields obtained by them being approximately 10 per cent.

Several patents have been taken out covering the production of isoprene from turpentine. Woltereck[12] passes the vapors of turpentine through an iron tube filled with contact material such as wire gauze, perforated disks, or similar material. The optimum temperature for the production of isoprene is said to be

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[1] *Ann. chim. phys.* [3], **39**, 5.

[2] *Ber.*, **9** (1876), 1991; *Z. Chem.* [2], **4**, 380.

[3] *Ber.*, **10** (1877), 113.

[4] *J. Chem. Soc.*, **45** (1884), 410; *Chem. News*, **46** (1882), 120.

[5] *Trans. Roy. Soc. London*, **1860**, 241.

[6] *Chem. News*, **65** (1892), 265.

[7] *Ann.*, **383** (1911), 228.

[8] THIS JOURNAL, **6** (1914), 803.

[9] *Ber.*, **44** (1911), 2212.

[10] D. R. P. 260,934; U. S. Patent 1,057,680.

[11] THIS JOURNAL, **11** (1915), 924.

[12] Brit. Patent 27,908 (1909).

TABLE I

RUN NO.	KIND OF TURPENTINE	Fraction Taken ° C.	Contents of Tube	Temperature of Tube ± 20° C.	Temperature of Vapor in Flask ° C.	Time of Run Hrs.	Isoprene Fraction up to 50° C. G.	Distillate above 50° C. G.	Residue G.	Gas Plus Loss G.	Isoprene G.	Isoprene Per cent
6	"Newport" Wood Turpentine	150–180	Empty	450	156–205	3.75	0	172	0	18	0.0	0.0
7	"Newport" Wood Turpentine	150–180	Empty	500	156–200	3.50	6	124	25	45	1.5	0.75
8	"Newport" Wood Turpentine	150–180	Empty	550	155–200	3.50	17	97	33	53	6.0	3.0
9	"Newport" Wood Turpentine	150–180	Empty	600	155–200	3.00	47	68	34	51	9.0	4.5
10	"Newport" Wood Turpentine	150–180	Empty	650	155–200	3.50	42	59	30	69	5.5	2.7
11	"Newport" Wood Turpentine	150–180	Empty	700	155–200	2.50	64	20	37	79	5.0	2.5
12	"Newport" Wood Turpentine	150–180	Porcelain[1]	600	154–200	3.25	40	54	31	75	8.0	4.0
13	Gum Turpentine	150–160	Porcelain	600	155–159	3.25	50	45	35	70	10.0	5.0
14	"Newport" Wood Turpentine	150–180	Porcelain	600	155–200	2.75	19	126	0	55	8.7	4.4
15	Distillate above 50° C. from Run 14	....	Porcelain	600	152–235	2.50	0	89	18	19	0.0	0.0
22	"Newport" Wood Turpentine	150–180	Porcelain	350	157–200	2.50	0	176	0	24	0.0	0.0
23	"Newport" Wood Turpentine	150–180	Porcelain	400	157–200	1.25	7	179	0	14	1.0	0.5
24	"Newport" Wood Turpentine	150–180	Porcelain	450	155–210	1.25	20	144	0	36	5.0	2.5
25	"Newport" Wood Turpentine	150–180	Porcelain	500	157–190	1.25	50	102	0	48	8.7	4.4
26	"Newport" Wood Turpentine	150–180	Porcelain	550	157–165	1.00	54	90	?	56	8.0	4.0
27–31	"Newport" Wood Turpentine	....	....	500	.....	...	..	...	..	..	128.0	4.6[2]
32	"Newport" Wood Turpentine	Not fractionated	$CuO.CuCl_2$	300	.....	...	..	...	..	..	128.0	...
33	"Newport" Wood Turpentine	Not fractionated	$CuO.CuCl_2$	400	157–185	1.50	6	100	94	..	...	...
34	"Newport" Wood Turpentine	Not fractionated	$CuO.CuCl_2$	400	157–200	1.00	3	189	8	..	...	...
35	"Newport" Wood Turpentine	Not fractionated	$CuO.CuCl_2$	450	160–220	1.50	11	174	15	..	3.0	1.5
36	"Newport" Wood Turpentine	Not fractionated	$CuO.CuCl_2$	500	158–210	2.50	22	132	46	..	4.0	2.0
37	"Newport" Wood Turpentine	Not fractionated	$CuO.CuCl_2$	550	156–210	2.00	34	110	56	..	5.0	2.5
38	"Newport" Wood Turpentine	Not fractionated	$CuO.CuCl_2$	600	155–215	2.50	48	81	71	..	5.0	2.5
39–40	"Newport" Wood Turpentine	Not fractionated	$CuO.CuCl_2$	650[4]	.....	...	..	...	..	..	...	...
45	Gum Turpentine (Commercial)	Not fractionated	Empty[5]	450	160–205	2.75	..	134.3	18	47.7	1.5	0.75 (?)
46	Gum Turpentine (Commercial)	Not fractionated	Empty	500	157–180	2.75	..	145.0	17.1	38.8	0.9	0.5 (?)
47–53[3]	Gum Turpentine (Commercial)	Not fractionated	Empty	450	157–200	14.33	671.9	1628.6	8.7	370.3	139.4	4.98[2]

[1] Small pieces of unglazed porcelain were used.
[2] Average.
[3] Total quantities for seven runs are given.
[4] Carbonization caused the tube to become plugged.
[5] Iron tube.

550° C., unless the vapors are diluted with an inert gas such as nitrogen, when a temperature of 600° C. is required. Heinemann[1] passed turpentine vapors over finely divided and heated copper or silver, or through a heated structure of these metals. With copper a temperature of about 480° C. is required, while with silver the optimum temperature is about 450° C. No figures on the yields are given. If the vapor is diluted with steam and the temperature of the tube raised to 750° C. a yield of 40 to 50 per cent of the material used is said to be obtained in the form of hydrocarbons boiling below 100° C., two-thirds of which is isoprene.[2]

Gross[3] claims to have obtained increased yields of isoprene by "cracking" turpentine in the presence of metals, metallic oxides, or mixtures of oxides and chlorides as catalysts at temperatures of 264° to 700° C. With copper oxide the effect is said to be apparent at 260° C. and is maximum at 305° C., when a yield of 35 per cent of isoprene is obtained. With copper as a catalyst, 500° C. is the optimum temperature, and a yield of 17.5 per cent is obtained.

From an examination of the literature it is apparent that data on the variation of the percentages of different products formed with change in temperature by "cracking" turpentine are rather meager, and that in most of the work no record of temperature has been made. The present work was undertaken for the purpose of investigating this variation, particularly with reference to the yields of isoprene and toluene, since the dibromide of the former has promise of being a suitable lachrymatory gas and the latter is needed in increasing quantities for the manufacture of the high explosive, trinitrotoluene.[4]

EXPERIMENTAL[1]

The type of apparatus used throughout the work is shown in Fig. 1. In Runs 1 to 44, inclusive, the heating unit consisted of a pyrex glass tube 26 mm. in diameter and wrapped for one meter of its length with 24 B and S gage nichrome wire. In all subsequent runs an iron tube of the same dimensions and similarly wrapped was used. The water in the Hopkins condenser was maintained at 50° C., so that the low boiling products passed through this condenser, and were subsequently cooled in the spiral condenser, and a spiral glass tube surrounded by a freezing mixture, and collected in a series of three receivers, one of which contained carbon tetrachloride, cooled in a freezing mixture. The high boiling products were condensed in the Hopkins condenser and allowed to run back to the distilling flask or trapped off as desired. Two hundred grams of turpentine were used in each run.

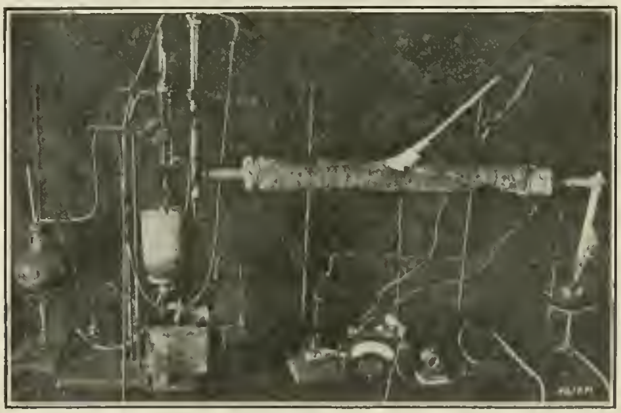

FIG. 1

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[1] Brit. Patents 14,040 and 24,236 (1910).
[2] Brit. Patent 1953 (1912).
[3] U. S. Patent 1,099,498.
[4] The work reported in this paper was begun in October 1917.

[1] Acknowledgment is made to Messrs. R. E. Kremers and D. E. Cable for assistance in this work.

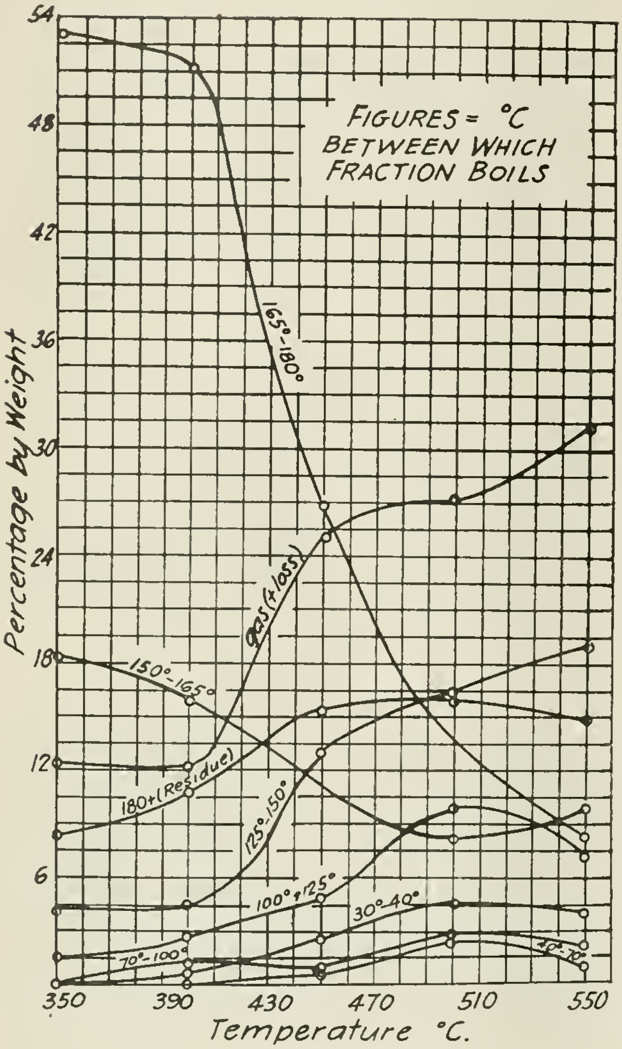

Fig. 2

The isoprene fraction was immediately distilled through a 12-in. Hempel column containing glass beads, and the portion boiling between 30° and 40° was taken as isoprene, since practically all of this portion on redistillation boiled between 35° and 37°. No attempt was made to determine the amount of trimethylethylene that may have been present in the isoprene. The results of some typical series of runs are given in Table I.

In Runs 6 to 11 the vapors were passed through the tube repeatedly, the high boiling distillate being allowed to return to the distilling flask. It was observed, however, that decreasing amounts of low boiling products were formed as the distillation proceeded. Subsequently it was shown (Runs 14 and 15) by passing the vapors through the heated tube once and then passing the distillate boiling at more than 50° through the tube again, that all of the isoprene obtained is formed during a single passage of the vapors through the tube. Accordingly, in all subsequent runs recorded in this table, the vapors were passed through the tube but once.

With an empty glass tube a maximum yield of isoprene is obtained at 600°, while with the same tube filled with porcelain 500° appears to be the optimum temperature. With the tube filled with a mixture of copper oxide and copper chloride prepared according to the patent issued to Gross,[1] no effect whatever in increasing the yield of isoprene was apparent.

Using an iron tube containing no contact material, the most suitable temperature for the production of isoprene appears to be 450°.

According to Harries,[1] the production of isoprene from turpentine is due to the presence of limonene (dipentene) in the turpentine. Wood turpentine, which contains considerable limonene,[2] might therefore be expected to give a larger yield of isoprene than gum turpentine. Results obtained in Runs 12 and 13 do not, however, confirm this.

The high boiling distillate and that portion of the isoprene distillate boiling above 40° were fractionated twice, using a 12-in. Hempel column filled with glass beads. The results obtained with the distillate secured in Runs 22 to 26 are typical, and are given in the form of curves in Fig. 2. Complete analyses of the various fractions were not made, but qualitative tests showed considerable quantities of terpenes in the higher boiling fractions obtained in "cracking" at the lower temperatures, while hydrocarbons of the benzene series and olefinic hydrocarbons are the chief constituents of all fractions at "cracking" temperatures over 400°.

The yields of the fractions boiling under 125° C. reach a maximum at 500°, as does the residue remaining at 180°, while the fraction boiling at 125° to 150° and the gas formed during the "cracking" process continue to increase with increase in the cracking temperature.

By means of its 2,4-dinitro compound[3] (m. p. 70° to 71°), toluene was found to be a chief constituent of the fraction boiling at 100° to 125°. The fraction boiling between 125° and 150° when tested for *m*-xylene gave a trinitro derivative melting at 175° to 176°. The melting point of pure trinitroxylene is 181° to 181.5°. The acid obtained by oxidizing a portion of the fraction boiling between 165° and 180° gave a dimethyl ester melting at 138°. Cymene under the conditions of the test gives dimethyl terephthalate which melts at 140°. The fraction boiling at 150° to 165° upon similar treatment gave a dimethyl ester melting at 55° (dimethyl isophthalate melts at 64°), indicating *m*-xylene and probably other *m*-compounds of the benzene series as constituents of this fraction.

The gas formed has an odor somewhat similar to that of coal gas and burns with a luminous flame. When placed in contact with fuming sulfuric acid, 10 to 22.5 per cent by volume dissolves, showing olefines present to that extent.

Since, according to the literature, larger yields of isoprene appear to be obtainable from limonene than from other terpenes, experiments were carried out in which turpentine was treated so as to convert the pinene into limonene before "cracking." According to

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[1] *Loc. cit.*

[2] Forest Service, *Bulletin* **105** (1913).

[3] Mulliken, "Identification of Pure Organic Compounds," **1** (1908), 202.

Wallach,[1] pinene is converted into limonene by prolonged heating at 250° to 270°. Several experiments were run in which the vapor of gum turpentine was passed through the iron tube heated to the above temperatures for from 2 to 20 hrs., and the material then "cracked" at 450°. The effect of this preliminary treatment is shown by the boiling-point curves in Fig. 3. The original turpentine which consists largely of pinene is converted into a more complex and higher boiling mixture of which limonene is a chief constituent. There was, however, no appreciable increase in the yield of isoprene upon "cracking" this product by passing it through the tube at the higher temperature. Activated coconut shell charcoal used as contact material in one run appeared to have no appreciable effect on the yield of isoprene.

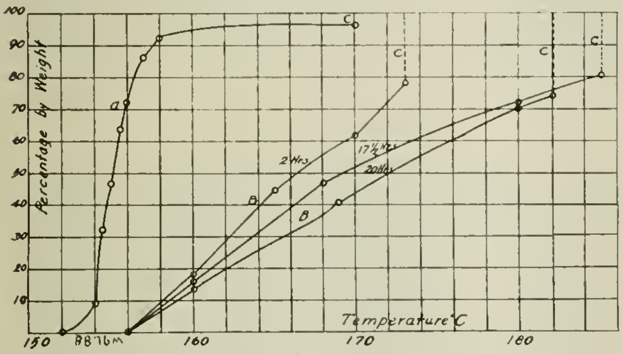

FIG. 3

A—Boiling-Point Curve of Original Turpentine. B—Boiling-Point Curve of Product after Heating at 250° to 270° C. for Time Indicated. C—Residue

The isoprene obtained in various runs was diluted with an equal volume of ether, the mixture well cooled, and the calculated amount of bromine required to give the dibromide added gradually, and the reaction mixture constantly agitated. The reaction was very violent at first but moderated after about one-half of the bromine had been added. The mixture separated a small amount of tar at first and gradually became darker, but no free bromine was apparent. When fractionated under reduced pressure the resulting product gave a 50 per cent yield of a product boiling at 76° to 104°, under approximately 18 mm. of pressure. The boiling point of isoprene dibromide[2] at 18 mm. is given as 101°. As reported by previous experimenters[3] this material has a marked irritating effect upon the mucous membrane. Tests after long standing, however, show that the material gradually loses its efficiency, probably by polymerization. This tendency would render it unfit for use as a lachrymatory gas unless a stabilizing agent could be found.

CONCLUSION

Although turpentine is a possible source of toluene in case of an emergency, it does not give, under the experimental conditions described in this paper, a sufficiently large yield of either toluene or isoprene to make it a practical source of these products under ordinary conditions.

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[1] *Ann.*, **227**, 282.

[2] *Bull. soc. chim.* [3], **35**, 989.

[3] *Chem. Zentr.*, **1899**, Part 1, 590

THE AGING OF CERTAIN RUBBER COMPOUNDS[1]

By I. R. Ruby and Harlan A. Depew

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Received September 4, 1920

There has been much discussion as to the relative merits of carbon black and zinc oxide treads for automobile tires. The outstanding objection to the black tread tire is that, although in the beginning it wears comparatively well, as time goes on the tread chips away at an accelerated rate.

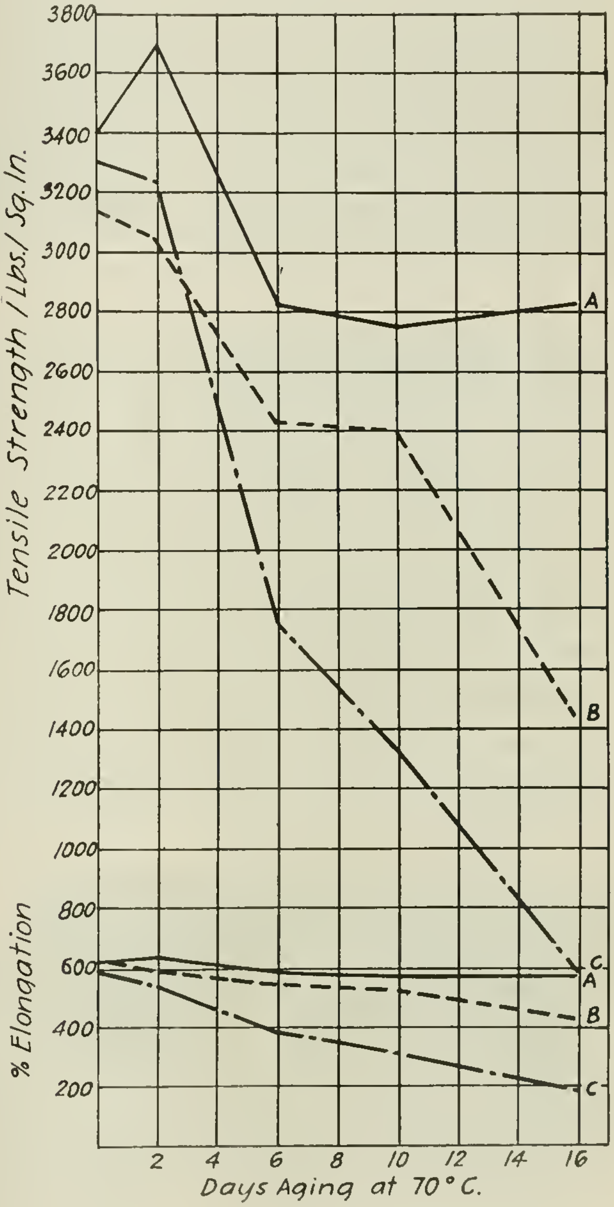

FIG. 1

To help analyze this difficulty three compounds, A, B, and C, were investigated. Table I gives their composition by weight and also by volume.

These compounds are typical fast-curing tread compounds, with the exception of A, which contains a low percentage of pigment. Treads in which XX Red zinc oxide is the only reinforcing pigment generally carry 55 to 58 per cent of zinc oxide instead of only 46 per cent, as in this case. There is no appreciable difference in aging, however, between compounds containing 46 and 58 per cent zinc oxide, as shown by evidence not included in this report.

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[1] Presented before the Rubber Division at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920

TABLE I—COMPOSITION OF COMPOUNDS

	By Weight			By Volume		
	A	B	C	A	B	C
First later	92	92	92	100	100	100
Sulfur	5.5	5.5	5.5	2.67	2.67	2.67
Hexamethylenetetramine	1.5	1.4	1.4	1.38	1.25	1.25
XX Red zinc oxide	84	98	22	15.0	17.5	4.0
Carbon black	..	..	25	..	..	14.5
Lithopone	..	20	..	..	5.0	..

The compounds were aged in an air bath at 70° C., as was suggested by Dr. Geer as an accelerated aging test. Tires, however, heat up from internal friction while running, and this temperature is often exceeded. In solid tires, in fact, the temperature at times exceeds 100° C.

The physical properties of the compounds after aging are tabulated in Table II.

TABLE II—PHYSICAL PROPERTIES OF THE COMPOUNDS ON AGING AT 70° C.

	0 Days		2 Days		6 Days		10 Days		16 Days	
Time of Cure 40 Lbs. Steam Min.	Tensile Strength Lbs. per Sq. In.	Elongation, Per cent	Tensile Strength Lbs. per Sq. In.	Elongation, Per cent	Tensile Strength Lbs. per Sq. In.	Elongation, Per cent	Tensile Strength Lbs. per Sq. In.	Elongation, Per cent	Tensile Strength Lbs. per Sq. In.	Elongation, Per cent
Sample A										
45	3410	626	3702	639	2832	591	2761	576	2831	577
60	3594	645	3605	563	2849	544	1322	330	2403	512
90	2764	495	2650	485	785	190	786	185	855	202
120	3154	564	1251	266	915	184	992	147	766	160
Sample B										
45	3144	629	3050	589	2435	544	2403	526	1445	429
60	3203	605	2708	538	1746	429	1525	394	588	170
90	2212	485	1396	359	844	197	740	169	504	100
120	1321	339	734	189	653	132	591	99	519	87
Sample C										
45	3306	585	3243	540	1763	386	1342	308	588	182
60	3408	577	3233	525	1087	263	1470	314	502	140
90	3808	652	1645	298	773	141	684	115	496	71
120	3217	566	1008	191	607	106	543	79	550	124

The aging for the forty-five minute cure is shown graphically in Fig. 1. Elongation is the typical property of rubber, and is a fairly satisfactory gage of the aging of its compounds.

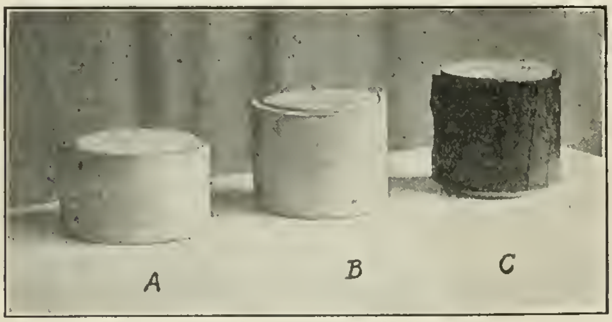

FIG. 2

It appears that the compound containing lithopone ages somewhat less satisfactorily than a straight XX Red zinc oxide compound. The carbon black compound is much inferior to the others on the basis of tensile strength and elongation on aging. This is especially serious when it is realized that, as the percentage of carbon black in a tread compound increases, the heat developed by internal friction increases faster than a linear function.

The test specimens were about 0.17 in. thick, and accordingly the tensile strength and elongation did not record an interesting hardening on the surface as fully as thinner specimens would have done. This hardening penetrated about 0 03 in. in 16 days. The effect is shown in Fig. 2, where the surface of the rubber compounded with carbon black is cracked deeply by bending the rubber. There is no evidence of this surface hardening in the case of Compounds A and B. This particular hardening is probably responsible to a considerable degree for the accelerated wear of a black tread tire with time, the hard surface being continually cracked and torn away by the road abrasion.

The cause is uncertain, but appears to be oxidation. The adsorptive power of carbon for oxygen has been recognized for some time, and it may be reasoned that the carbon black acts as a catalyst and oxidizes the soft rubber to a hard rubber.

SOME MICROSECTIONS CUT FROM VULCANIZED RUBBER ARTICLES[1]

By Harlan A. Depew and I. R. Ruby

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Received September 4, 1920

It has long been recognized that pigments for use in rubber work should consist of very fine particles.

Microscopic work done in this laboratory on pigments in linseed oil and other paint vehicles has shown that fine particles tend to exist as flocculates. In certain vehicles this flocculation is largely or entirely overcome. In the case of water suspensions, as well as of paints, the physical properties of a deflocculated and a flocculated suspension differ greatly.

Carrying the suspension analogy still further to the very much more viscous (properly, plastic) medium, rubber, it seems reasonable to assume that dispersion and flocculation of pigments play important parts in determining the physical properties of compounded rubber.

Attempts to determine the dispersion of pigments in compounded rubber by reflected light have failed, because with the high magnifying powers necessary to see the individual particles of, for example, zinc oxide or carbon black, the illumination of the surface is entirely too weak, particularly where the reflecting properties of the medium and the suspended pigment are close. Our success with transmitted light in water and oil suspensions pointed to this method of illumination for the examination of compounded rubber.

There is considerable difficulty in cutting sufficiently thin sections of vulcanized rubber, owing to its elasticity and toughness, especially in the case of rubber highly compounded with zinc oxide or carbon black, where the thickness must not exceed 1 μ. In less highly compounded matter the section can be 20 μ thick, or even thicker. The elasticity can be destroyed by immersing in liquid air, but this makes the sample too hard to cut. Accordingly, the rubber must be frozen to an extent just sufficient to destroy its elasticity and yet not make it too hard.

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[1] Presented before the Rubber Division at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

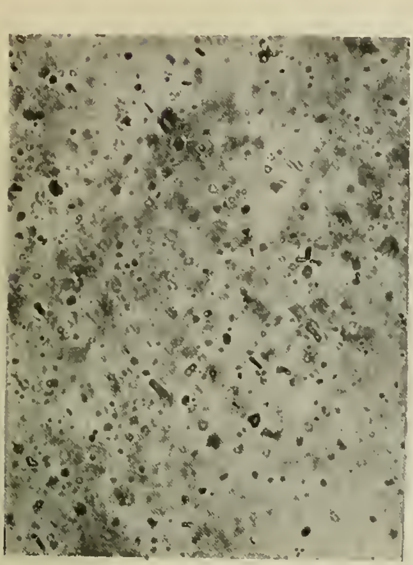

FIG. 1

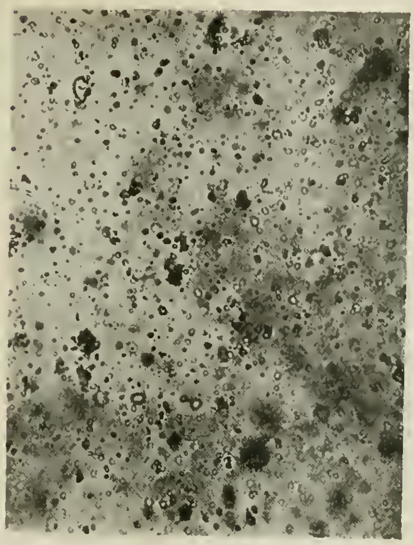

FIG. 2

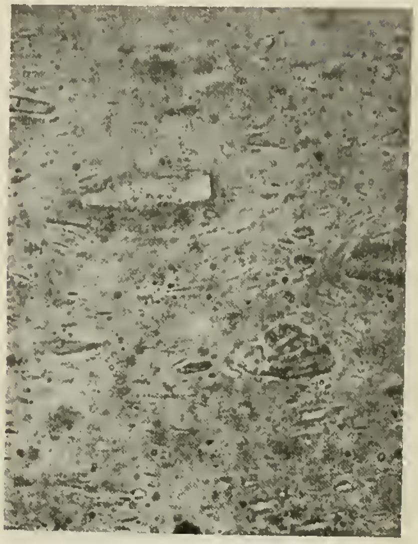

FIG. 3

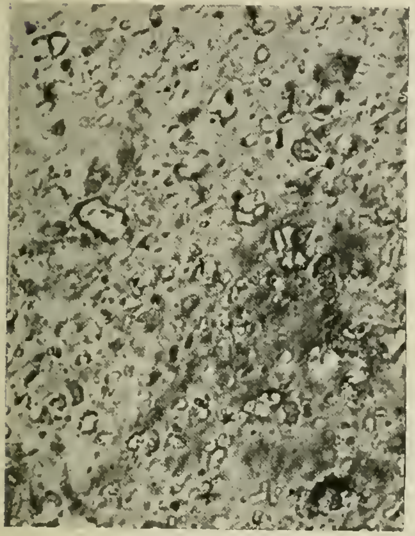

FIG. 4

FIG. 5

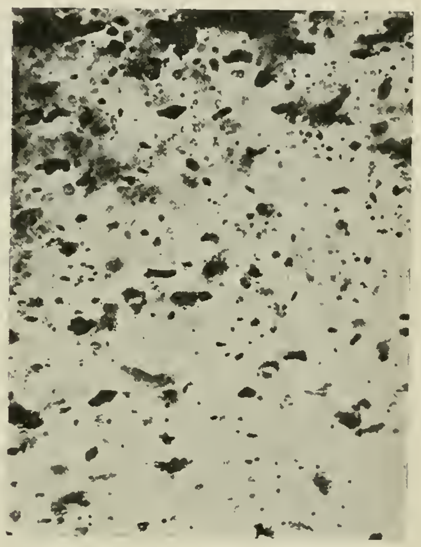

FIG. 6

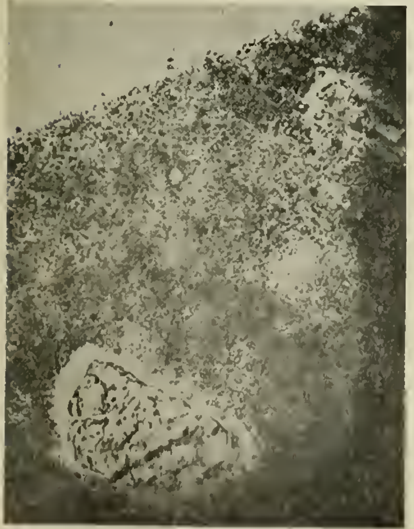

FIG. 7

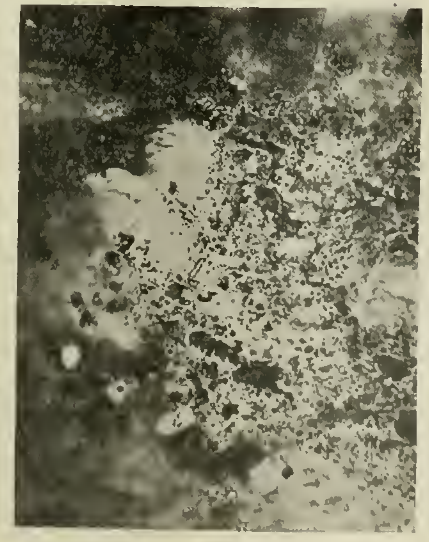

FIG. 8

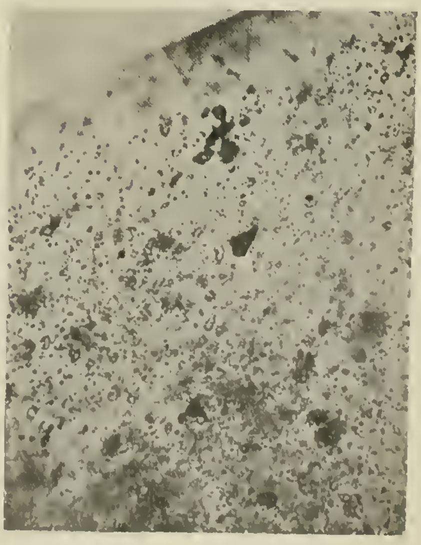

FIG. 9

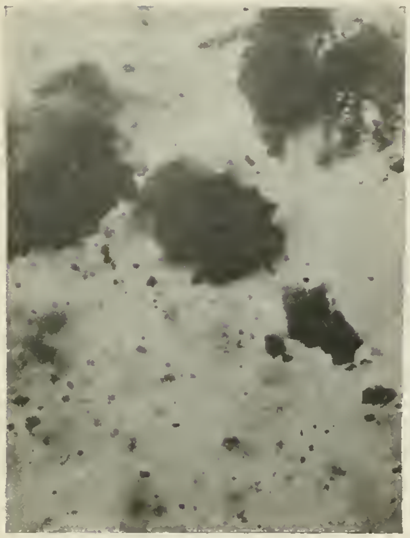

Fig. 10

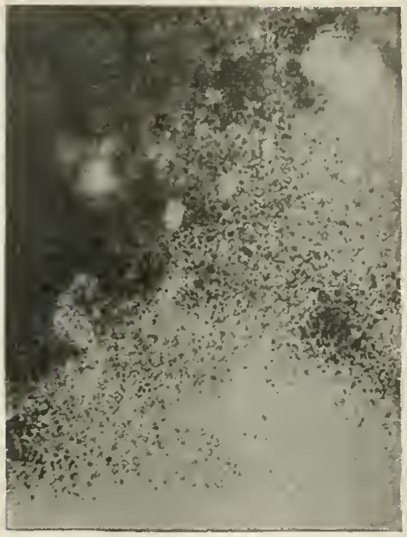

Fig. 11

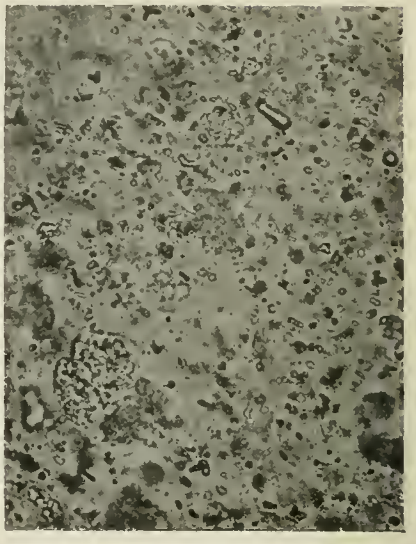

Fig. 12

Fig. 13

The method finally developed consists in freezing the rubber by expansion of carbon dioxide on the stage of an ordinary Spencer microtome. The sample is held tight on the stage by means of a water-glycerol solution (90 : 10) which, on cooling, solidifies to a white mass. This solution is used because it does not become very brittle at the low temperatures. The carbon dioxide does not cool the sample to a sufficiently low temperature, and a surface flash cooling is given by liquid air. The liquid air can be obtained at a convenient liquid air manufacturing plant and transported without difficulty in an "Icy-Hot" bottle, which will keep liquid air for several days. The liquid air may be ejected very satisfactorily from the bottle by introducing carefully a one-hole rubber stopper through which a glass tube about 3 to 4 mm. in diameter is passed into the bottle. The pressure developed by the continual evaporation will force a stream of the liquid out, which can be directed on the sample. A very small amount will freeze the sample sufficiently.

The section is then cut with the knife. Raising the stage is best controlled by hand. The thin section is mounted in Canada balsam on a microscope slide and preferably examined visually at 1500 diameters, using a Zeiss 2 mm. apochromatic oil-immersion lens. For photographing, sharper negatives are obtained at 800 diameters.

DESCRIPTION OF CUTS

In Fig. 1 zinc oxide is shown uniformly dispersed in rubber. A typical triplet crystal can be noted and also the grain in the rubber in the direction of working is shown by the definite alignment of the needle-shaped crystals.

In Fig. 2 a good lithopone is shown very well dispersed.

Fig. 3 contains aluminium flake. The grain is shown very decidedly, and it is not difficult to believe that the tensile strength and elongation will vary according to the direction of testing.

Fig. 4 shows whiting.

Fig. 5 is iron oxide. It is well dispersed but contains many large particles.

Fig. 6 was litharge when introduced and should have shown clear centered particles when in focus, but the particles have become black, due to a surface coating of sulfide.

Fig. 7 is a well-known white tread with magnesia as an accelerator. Chunks of magnesia stand out in sharp contrast to the uniform distribution of the zinc oxide. The individual particles of zinc oxide do not show up well except near the edge, owing to the thickness of the section which was necessary to show the large particles of magnesia.

Fig. 8 is a section from a widely advertised composition sole bought from a shoe repairman. It shows the iron oxide used in coloring, the zinc oxide used in reinforcing, and the fiber used for stiffening. The photograph is poor, but the section can be seen more distinctly by direct observation with the microscope.

Fig. 9 shows a zinc oxide tread with a very small amount of lampblack to give a gray color. The lampblack is badly flocculated.

Fig. 10 shows a poorly dispersed carbon black.

Fig. 11 shows a well-dispersed carbon black together with zinc oxide.

Fig. 12 is a section from the sidewall containing zinc oxide and whiting.

Fig. 13 is a section of a cushion from a tire made by a large manufacturer, showing reclaimed rubber and a small amount of zinc oxide.

Microscopic examination opens up the following possibilities:

(1) A knowledge of the dispersion of the pigment in rubber which will tell a good deal about the quality

of the product. Flocculated pigment can readily account for many difficulties otherwise inexplicable. Among these is the heating up of tire treads heavily compounded with carbon black.

(2) A help in the analysis of rubber goods by showing the compounding ingredients used, such as reclaimed rubber, fiber, and pigment. In the case of the pigment, it may even be possible to learn the source, because the same pigment made according to different processes varies greatly in shape and size. Chemical analysis shows no difference between blanc fixe and ground barytes, but the microscope tells at once.

Most work of this character is done by direct observation under the microscope without the trouble of photographing. By examining the slide with colored light, increased contrast is shown in certain cases. It is planned to make observations with polarized light, which should open a wide field for further investigation and for identification of the pigments. It should be mentioned also that staining of the section will bring out particles which would otherwise be invisible, as, for instance, glue.[1]

ACKNOWLEDGMENT

Acknowledgment is due to Messrs. Henry Green and Rodger Graver of our Microscopic Section for the photographs of the sections which have been shown with this paper.

THE SOLUBILITY OF METALS IN ACIDS CONTAINING FORMALDEHYDE

By Roger C. Griffin

Laboratories of Arthur D. Little, Inc., Cambridge, Mass.

Received June 21, 1920

At the Philadelphia meeting of the American Chemical Society the statement was made that a small amount of formaldehyde dissolved in a solution of hydrochloric acid would very greatly reduce solvent action of the latter upon steel. For certain purposes it seemed worth while to make a further investigation of this phenomenon in order to determine whether formaldehyde would have a similar inhibitory effect upon the solution of other metals by hydrochloric acid, and whether other acids would also behave in like manner.

We have accordingly carried through a series of tests with some of the more common metals and alloys, and, although an exhaustive study of the reaction has not been attempted, we believe that the results obtained will be of general interest.

MATERIALS

METALS—For purposes of record each metal was first subjected to chemical analysis, the results of which are given in Tables I and II.

Table I—Ferrous Metals (In Per cent)

Material	C	Mn	P	Si	S
Wrought Iron	0.01	0.02	0.230	0.13	0.023
Cast Iron	3.57[1]	0.62	0.489	1.82	0.081
Steel A	0.15	0.31	0.008	0.15	0.037
Steel B	1.06	0.27	0.019	0.02	0.029
Steel C	1.26	0.25	0.014	0.06	0.015

[1] Graphitic carbon 3.04 per cent; combined carbon 0.53 per cent.

ACIDS—The acids were J. T. Baker's C. P. products. The hydrochloric acid was about 17 per cent strength by weight, made by diluting the concentrated acid with an equal volume of distilled water. The sulfuric acid was 10° Bé., containing about 11 per cent sulfuric acid. The nitric acid was 10 per cent strength. In one case dilute aqua regia was employed, made by mixing 1 volume of concentrated nitric acid, 3 volumes of concentrated hydrochloric acid, and 36 volumes of distilled water.

METHOD OF TESTING

Most of the metals were in the form of sheets of varying thickness, which were cut into pieces about 1 in. square for the test. In the cases of the solder, wrought iron, and cast iron, it was necessary to use pieces of somewhat irregular shape. Each piece was carefully cleaned with emery cloth and then with ether or gasoline to remove any oil. The pieces were accurately weighed, and immersed in a considerable volume of the acid solution at room temperature for a definite length of time, after which they were withdrawn, rinsed with water, then with alcohol, dried without heat, and again weighed. Duplicate tests were carried out on each metal with the various acid solutions and also with the corresponding acid solutions to which was added 2.5 per cent by weight of commercial formalin (equivalent to 1 per cent of absolute formaldehyde). The corresponding tests with and without formaldehyde were conducted simultaneously in order that the temperature and volume conditions would be comparative for each.

The corrosion loss, K, was figured by the formula of R. B. Faher,[1]

$$K = \frac{PV}{A},$$

where P = percentage loss in weight, A = area of exposed surface in sq. cm., and V = volume of the specimen in cc. The area of the surface was computed from careful measurement, and the volume by weighing in air and then in water.

RESULTS OF TESTS

SULFURIC ACID—The results of the tests with 10° Bé. sulfuric acid are given in Table III. The tests with wrought iron, cast iron, and steel show that the addition of 1 per cent of formaldehyde to the sulfuric acid solution very greatly reduces the solvent effect of the acid. In the case of all the other metals the loss with the sulfuric acid was so small that it was not considered worth while to make the tests with the formaldehyde-acid mixture.

HYDROCHLORIC ACID—The results of the tests with 1 : 1 hydrochloric acid are shown in Table IV. The figures show that formaldehyde had a marked inhibitory effect on the action of 1 : 1 hydrochloric acid on wrought iron, cast iron, and steel. In the case of the other metals the differences were too small to be significant. The percentage variation between the effect of acid with and without formaldehyde was considerable in the case of the solder and the nickel, but the actual losses were so small that it does not

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[1] W. E. Wiegand, *Can. Chem. J.*, **4** (1920), 160.

[1] *J. Soc. Automotive Eng.*, **4** (1919), 42.

TABLE II—NON-FERROUS METALS (IN PER CENT)

MATERIAL	Cu	Fe	Pb	Sn	Zn	Mn	Sb	Ni	As
Brass	61.03	0.17	0.37	0.21	38.22[1]	..	..	..	..
Admiralty Metal	71.58	..	0.03	1.04	27.35[1]	..	..	..	..
Manganese Bronze	57.52	0.54	0.09	0.60	41.24[1]	0.01	..	..	..
Solder	..	..	49.11[1]	50.57	..	..	0.32	..	..
Nickel Silver	54.49	0.27	..	..	26.63[1]	..	..	18.61	..
Sheet Copper	99.86	..	..	..	..	..	..	..	..
Sheet Lead	..	..	99.82	..	..	..	..	..	..
Sheet Nickel	0.11	0.40	..	..	..	..	..	98.80	..
Sheet Tin	None	None	None	100[1]	..	..	None	..	None

[1] By difference.

seem safe to draw definite conclusions without further confirmation.

TABLE III—WITH 10° BÉ. SULFURIC ACID

MATERIAL	Time Min.	K		Decrease Per cent
		Without Formaldehyde	With Formaldehyde	
Wrought Iron	3	0.007	0.001	—86
Wrought Iron	60	0.190	0.010	—95
Cast Iron	2	0.007	0.0025	—65
Cast Iron	60	0.301	0.039	—87
Steel A	60	0.036	0.004	—89
Steel B	60	0.063	0.004	—98
Steel C	60	0.008	0.001	—88
Brass	480	0.002	0.001	..
Admiralty Metal	480	0.001	..	..
Manganese Bronze	480	0.002	..	..
Copper	480	0.001	..	..
Tin	480	0.003	0.003	..
Solder	60	0.001	..	..
Nickel Silver	60	0.0007	0.0000	..
Nickel	480	0.002	0.001	..

TABLE IV—WITH HYDROCHLORIC ACID (1 : 1)

MATERIAL	Time Min.	K		Increase or Decrease Per cent
		Without Formaldehyde	With Formaldehyde	
Wrought Iron	2	0.010	0.005	—50
Wrought Iron	15	0.026	0.005	—81
Cast Iron	2	0.018	0.005	—72
Cast Iron	60	0.111	0.075	—32
Steel A	60	0.037	0.005	—87
Steel B	60	0.032	0.006	—81
Steel C	60	0.009	0.005	—55
Brass	480	0.0025	0.002	..
Admiralty Metal	480	0.0015	..	..
Manganese Bronze	60	0.001	0.001	..
Manganese Bronze	480	0.003	0.002	..
Tin	60	0.002	0.001	..
Tin	480	0.007	0.005	..
Solder	20	0.002	0.001	..
Solder	60	0.003	0.008	+167
Nickel	480	0.007	0.0035	—50

NITRIC ACID—Table V shows the results of the tests with 10 per cent nitric acid. The results with this acid are in some cases rather contradictory. It seems probable that there may be some reaction between the formaldehyde and nitric acid or nitric oxide, thus introducing a disturbing factor. Another difficulty with this series of tests was that the reaction in some cases was rather violent, causing a heating of the solution. In general, the presence of formaldehyde seems to retard the action of the acid, but, before definite conclusions can be drawn, the reactions with this acid need further study under careful temperature control.

TABLE V—WITH 10 PER CENT NITRIC ACID

MATERIAL	Time Min.	K		Increase or Decrease Per cent
		Without Formaldehyde	With Formaldehyde	
Wrought Iron	5	0.248	0.152	—39
Cast Iron	3	0.158	0.013	—92
Cast Iron	20	0.298	0.212	—29
Steel A	60	0.572	0.566	..
Steel B	2	0.096	0.083	—14
Steel B	10	0.352	0.275	—22
Steel C	2	0.157	0.136	—13
Steel C	5	0.237	0.134	—43
Brass	480	0.090	0.028	—69
Admiralty Metal	60	0.004	0.002	—33
Admiralty Metal	480	0.110	0.248	+126
Manganese Bronze	60	0.012	0.001	—92
Manganese Bronze	480	0.244	0.122	—50
Copper	60	0.049	0.009	—92
Copper	480	0.120	0.103	—6
Lead	30	0.119	0.127	..
Lead	480	0.249	0.241	..
Tin	60	0.086	0.052	—40
Tin	120	0.153	0.138	—10
Solder	20	0.181	0.125	—31
Solder	60	0.217	0.421	+94
Nickel Silver	60	0.010	0.001	—90
Nickel	60	0.007	0.005	—30
Nickel	480	0.028	0.004	—86

AQUA REGIA—A test was made with dilute aqua regia upon wrought iron with the following results:

	Time Min.	K		Decrease Per cent
		Without Formaldehyde	With Formaldehyde	
Wrought iron	60	0.039	0.009	—77

The presence of formaldehyde appears to decrease the effect of dilute aqua regia upon wrought iron.

PRACTICAL APPLICATION

Recently there were submitted to this laboratory samples of rusty steel rods which it was desired to free from the rust without hurting the underlying steel. When the rods were treated with 1 : 1 muriatic acid containing about 1 per cent of formaldehyde, the rust was completely removed without any visible pitting of the steel.

SUMMARY

The above tests were carried out principally to learn whether the presence of a small amount of formaldehyde in various acids would have a marked effect in decreasing their solvent action upon steel, iron, and other metals. The results show that the presence of 1 per cent of formaldehyde in a 10° Bé. sulfuric acid solution and also in a 1 : 1 hydrochloric acid solution decreases the solvent action of these acids upon wrought iron, cast iron, and steel to a remarkable degree. The effect in the case of the other metals tested was not sufficient to be important for the purposes of this investigation. The effect is less marked with 10 per cent nitric acid, possibly on account of secondary reactions.

The use of muriatic acid containing about 1 per cent of formaldehyde affords a convenient means of pickling rusty steel without appreciably affecting the surface of the steel itself.

THE ACID HYDROLYSIS OF SUGAR-CANE FIBER AND COTTONSEED HULLS[1]

By E. C. Sherrard and G. W. Blanco

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In connection with the investigations of the Forest Products Laboratory during the war upon the preparation of ethyl alcohol from wood, it became desirable to apply the same treatment to sugar-cane fiber and cottonseed hulls. Although these waste materials contained a relatively large proportion of cellulose, it was found that only a small quantity of fermentable sugar was formed by hydrolysis, and that xylose constituted the largest part of the sugars thus produced.

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[1] Presented before the Division of Industrial and Engineering Chemistry at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

SUGAR-CANE FIBER

Previous investigators have obtained xylose from this material by first extracting with a dilute alkali and then hydrolyzing the extract with a dilute acid at atmospheric pressure. H. C. Prinsen-Geerligs[1] has thus obtained 30 per cent xylan, which upon hydrolysis with dilute acid yielded 79 per cent of sugar, a part of which was xylose. Since crystals of this sugar gave a specific rotation of +20°, he concluded that "probably some other sugar with a higher rotatory power was present, perhaps arabinose or *d*-glucose, resulting from the hydrolysis of the cellulose." C. A. Browne[2] used the same method and obtained a yield of cane gum corresponding to 25 per cent of the original fiber. This upon hydrolysis with dilute acid yielded 27.61 per cent of its weight of xylose. Based upon the dry weight of the original fiber, this would correspond to a yield of 6.68 per cent. The latter figure represents the quantity actually obtained as crystalline xylose and is necessarily lower than the actual yield. He was also able to show the presence of a small quantity of arabinose in the mother liquor remaining after the isolation of the xylose.

The present investigation deals with the direct hydrolysis of crude bagasse, using the method and apparatus previously employed for the study of the hydrolysis of wood.[3] The process consists of digesting 25 to 100 lbs. of the material in a rotating digester with 1.8 to 2.5 per cent of sulfuric acid for 17 to 50 min. at a pressure of from 100 to 125 lbs. After blowing off to atmospheric pressure the material is centrifuged and the remaining sugar extracted in leaching towers. The liquors are then mixed, the acid neutralized with calcium carbonate, and the whole evaporated to a liquor suitable for fermenting, *i. e.*, a solution having a sugar content of 5 to 7 per cent. The total reducing sugars thus produced are determined by means of Fehling's solution. The copper oxide formed is redissolved in nitric acid, and the copper deposited electrolytically. The sugar yields from cane fiber produced in this way are comparable with those obtained from a similar treatment of coniferous wood; in fact, they are somewhat greater than those obtained from a standard wood such as longleaf pine or white spruce.

In view of the fact that bagasse contains from 50 to 55 per cent of cellulose, one would expect the formation of considerable quantities of fermentable sugar when subjected to a digestion under the above conditions. Such, however, was not the case; the average of nine fermentations showed only 24.16 per cent of fermentable sugar as determined from the quantity of sugar removed, and of this only 50 to 60 per cent was obtained as alcohol. That the presence of hydrolytic products did not interfere with the action of the yeast during fermentation was demonstrated by fortifying the liquor with pure molasses such as was used in the propagation of the yeast. Here the fermentation took place readily and with an alcohol yield commensurate with the quantity of molasses added.

When it was found that the fermentable sugar constituted a relatively small portion of the total sugars, an effort was made to isolate and identify the nonfermentable reducing substances. The attempt, however, was not successful, since the large quantities of gum in the liquor prevented the crystallization of the sugars, although every means was utilized to clarify and purify this liquor.

In order to obtain a liquor from which crystals could be obtained resort was had to Hudson's method for the preparation of xylose from corncobs.[1] One hundred grams of bagasse having a moisture content of 7.48 per cent were first extracted for 24 hrs. at room temperature with 3120 cc. of a 2 per cent solution of ammonium hydroxide. The ammoniacal liquor was then pressed out and the residue washed with cold water.

The ammonia extraction removed 15 per cent of the original dry material. This extract after acidification did not reduce Fehling's solution. It was then hydrolyzed by boiling with a 4 per cent solution of sulfuric acid, but still no reduction of Fehling's solution was noted. Upon evaporation the ammoniacal liquor deposited a hard, brittle residue.

The extracted cane fiber was then digested with 2 liters of 7 per cent sulfuric acid for 2 hrs., pressed, washed, and dried. This treatment removed 35.8 per cent of the residue remaining from the ammonia extraction. The total reducing substances present in this acid liquor corresponded to 21.22 per cent of the original dry fiber. After neutralization and clarification, the liquor was evaporated under reduced pressure to a thick sirup, and crystallization started by the gradual addition of 95 per cent alcohol. Two crops of crystals were obtained from this liquor, both of which showed a melting point of 139° and gave osazones which melted at 160° and 159°, respectively, and formed the characteristic boat-shaped crystals of the double salt of cadmium xylonate and bromide. The crystals were strongly multirotatory and showed specific rotation of +18.2°. In all, 11.2 g. of pure crystals of xylose were obtained. This is equivalent to 12.1 per cent of the original dry fiber, or to 57.0 per cent of the total sugar determined by means of Fehling's solution. No doubt the mother liquor contained much more xylose, although all efforts to produce further crystallization were futile. Due to lack of time the mother liquor was not investigated further.

COTTONSEED HULLS

Cottonseed hulls were subjected to the same high pressure treatment as was bagasse, and the same difficulty was encountered in obtaining crystals from the liquor. It will be noted in Table I that the sugar determined by means of Fehling's solution is much less than was obtained from bagasse. This is due to the hard, brittle nature of the material and the difficulty of penetration. That the penetration is small is shown by the fact that the digested material contained only 56.89 per cent of moisture after a 50-min. cook. Here again little or no fermentation took place when the liquor was seeded with a pure yeast culture.

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[1] "Observations in Bagasse," *Sugar Cane*, **30**, 91.

[2] *J. Am. Chem. Soc.*, **26** (1904), 1221.

[3] Kressman, This Journal, **7** (1915), 920.

[1] *J. Am. Chem. Soc.*, **40** (1918), 1601.

Table I—Digester and Fermentation Record

Material	Cook No.	Pressure, Lbs. per Sq. In.	Tine of Cooking Min.	Maximum Temperature, ° F.	Water, Per cent of Dry Material	Acid, Per cent of Dry Material	Dry Wt. of Material, Lbs.	Moisture in Material as Charged	Digested Material Lbs.	Moisture in Digested Material	Dry Wt. Digested Material, Lbs.	Total Reducing Sugar, Per cent of Dry Original Material	Per cent Total Reducing Sugar Fermentable	Alcohol, Per cent by Weight	Theoretical Alcohol, Per cent by Weight	Average Number Fermentation	
Bagasse	B-2	107.5	30	320	125	2.50	62.55	40.0	226.39	77.1	51.85	22.4	25.5	0.48	0.937	3	
Washed bagasse	B-3	120.0	25	332	250	2.13	39.55	69.4	227.35	85.5	32.96	27.3	23.3	0.496	0.782	2	
Bagasse	B-4	107.0	17	319	125	1.92	65.5	40.1	257.5	74.1	66.7	26.7	18.7	0.560	0.735	1	
Bagasse	B-5	100.0	45	310	125	2.00	36.36	49.5	93.65	69.45	28.61	27.3	.....	.....	.....	1	No fermentation
Bagasse	B-6	100.0	50	310	125	2.00	29.95	52.27	91.95	71.76	26.40	27.4	.....	.....	.....	.	
Cottonseed hulls	114	120	28	334	100	1.80	95.06	4.94	214.7	59.29	87.41	9.6	None	.....	.....	3	Preliminary cook
Cottonseed hulls	115	120	28	328	100	1.80	95.06	4.94	151.5	56.79	65.46	13.9	None	.....	.....	2	Valve clogged blow off 55 min.
Cottonseed hulls	119	120	35	334	125	1.80	76.4	4.50	116.97	59.36	47.53	16.7	None	.....	.....	2	
Cottonseed hulls	131	100	58	310	125	2.00	90.48	9.52	127.0	56.89	54.75	13.8	None	.....	.....	.	

The difficulty of obtaining crystals was overcome by first extracting with dilute ammonia and hydrolyzing with 7 per cent sulfuric acid as described by Hudson and Harding.[1] This method gave excellent results, and yields corresponding to those of the original article were obtained. Polariscopic determinations were made upon these crystals and the results compared with those of the xylose obtained from bagasse. The similarity of the multirotations exhibited by xylose obtained from the two sources may be seen from Table II.

Table II—Polarization of Xylose from Bagasse and Cottonseed Hulls at 26° C.

Xylose from Bagasse		Xylose from Cottonseed Hulls	
Time Min.	Polariscope Reading ° V.	Time Min	Polariscope Reading ° V.
10	9.8	10	10.2
20	7.0	20	7.0
30	5.0	31	5.0
40	4.2	35	4.0
50	3.9	51	3.8
60	3.6	61	3.6
70	3.5	73	3.5
157	3.6	155	3.6

The final reading in both cases corresponds to a specific rotation of 18.03° which agrees fairly well with that calculated according to Tollens, formula: $[\alpha]_D$ = 18.337°. (Schultze and Tollens, *Ann.*, **271**, 40.)

CONCLUSIONS AND SUMMARY

It has been demonstrated that bagasse and cottonseed hulls without previous treatment are unsuitable for the preparation of ethyl alcohol. Of the total sugars produced by the acid hydrolysis of these materials, only a small quantity is fermentable, the larger proportion being of the pentose variety.

The fact that two cellulose-containing materials, such as bagasse and cottonseed hulls, produce xylose and almost no fermentable sugar upon digestion with dilute sulfuric acid indicates that a pentose sugar may influence the equilibrium finally established in the hydrolysis of cellulose to hexose sugars. Cahoe[2] has pointed out that under similar conditions wood will produce a maximum of 25 to 29 per cent sugar. Since Browne[3] showed by the use of concentrated acid that glucose could be obtained from the cellulose residue from cane fiber after the removal of the xylose, it is safe to conclude that the presence of a pentose interferes with the production of fermentable hexoses. In the case of cane fiber the maximum production of total reducing sugars was obtained, pentoses constituting by far the larger part of the total.

Attention is called to sugar-cane fiber or bagasse as a very promising source of xylose and furfural.

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[1] *J. Am. Chem. Soc.*, **39** (1917), 1038.

[2] *J. Soc. Chem. Ind.*, **31** (1912), 513.

[3] *Loc. cit.*, p. 1232

STUDIES ON TECHNICAL CASEIN. I—INTRODUCTION[1]

By W. Mansfield Clark

Research Laboratories of the Dairy Division, Bureau of Animal Industry, U. S. Department of Agriculture, Washington, D. C.

Received September 20, 1920

In July 1918 the United States Shipping Board invited a number of technical men to confer upon the prospective supply of casein. The annual requirement for the manufacture of waterproof glue used in airplanes was estimated by representatives of the Army and the Navy at 3,000,000 lbs. This requirement was exclusive of the ordinary demands of commerce, and concerned only the special grades demanded by glue manufacturers. These manufacturers claimed that Argentine casein was essential, and that stocks on hand would be exhausted by the following January. Further importations were to be stopped by the Shipping Board to release tonnage for other purposes, and it was therefore necessary to insure the entire future supply and especially the grades suitable for glue by domestic production. To meet this situation, the coöperation of the Dairy Division of the Department of Agriculture was asked.

The three following papers, describing an improved type of casein, a study of analytical control methods, and a development of the borax solubility test, report in part the work done by the Dairy Division.

In determining the course to follow, the Division considered a number of questions which it may be of value to recite briefly.

The Government had already adopted certain specifications for all casein going into glue for use in the manufacture of airplanes. An examination of the analyses of technical casein, which were later reported by Browne,[2] indicated that domestic methods of manufacture would provide no very great certainty of meeting the government specifications without careful selection. Another feature was the wide variation in the physical characteristics of various types of casein. The experience of the Forest Products Laboratory indicated a wide variation in the nature of various caseins, with the consequent necessity of altering glue formulas to meet these variations.[3] While the manufacturers of glue offered no clear reason for their insistence upon the one type of imported casein, it was reasonable to suppose that their experience had shown that good glues were obtained only when the glue formula was empirically adapted to the physical characteristics of the type of casein to which they had become accustomed. Since there were no well-grounded physical tests whose significance for glue manufacture had been demonstrated, and which could therefore be used in its control, it seemed imperative that the contemplated supply should be as nearly uniform as possible, not only in the analytical requirements of the government specifications, but also in physical characteristics.

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[1] Published by permission of the Secretary of Agriculture.

[2] This Journal, **11** (1919), 1019.

[3] S. Butterman, *Ibid.*, **12** (1920), 141.

The choice, then, lay between stimulating production according to methods in common use with selection of the better lots, and developing a procedure capable of control and certain to yield reliable material.

Of the methods in use, the so-called natural-sour method was at once ruled out as impracticably slow for those large factories where an adequate supply of milk would be available during the winter months. Such factories were manufacturing lactose, of which there was a shortage. Any method introduced would therefore have to conform to the necessities of lactose manufacture. The several methods in which high temperatures are used were rejected, for the simple reason that in the precipitation of casein at high temperatures several phenomena are involved which we know no way to control.

There remained the simplest of all methods, the precipitation of casein from relatively cool skim milk by mineral acids. Hydrochloric acid was indicated because the cheaper sulfuric acid leaves a precipitate of calcium sulfate which interferes with lactose isolation.

In its commercial application this simple procedure had often furnished the poorest of all grades of casein and was seldom conducted in a manner which gave uniform material. Van Slyke and Baker[1] had so improved the method that casein with remarkably low ash content and very promising physical characteristics had been produced on a large laboratory scale. Unfortunately, however, one of the distinct features of Van Slyke's method is the precipitation of the casein in a very finely divided form. This material could not have been handled in the quantities demanded with the equipment available at the factories or available by purchase during the disturbed conditions of 1918.

Judged by prevailing methods of manufacture, the chief point in casein manufacture seems often to have been to get the casein out of the way as rapidly as possible, and the casein was often precipitated in such a way that it would come together in large masses which could be forked out of the vat. The market price which has prevailed at times may have justified the handling of casein with regard only for economy of time and labor. On the other hand, it is possible that the uneven quality of commercial caseins resulting from such careless handling may have discouraged uses which might have created a better market for uniform and superior caseins. Be that as it may, the market price had been set under the influence of the conditions briefly touched upon above; and it was felt that if the government needs were to be supplied at a time when the market price was ascending, any serious increase in cost of production would not be looked upon with favor. It was, therefore, necessary to consider the prevailing habits of operation and the available equipment, and to avoid elaborate changes such as laboratory procedures might suggest. Therefore one of the chief requisites was a form of precipitate which could be handled with reasonable ease and rapidity.

The method described in the following paper was put into commercial operation under our supervision, and at the time the armistice was signed it was left in the hands of the men who had been instructed in its use. We understand that it is still in operation, although with what modifications, if any, we do not know.

That there was promise of meeting the volume requirements with this type of casein is indicated by the initial production of 150,000 lbs. during the first two months of operation.

That the product would surely and uniformly meet the analytical requirements demanded of all caseins destined to enter the glue of aircraft was very clearly indicated. Since the government specifications were chiefly concerned with the analytical qualities of caseins and since methods of analysis were in a somewhat uncertain state of development, a study of analytical methods was made, as reported by Mr. Shaw (Part III).

As mentioned before, it was considered very desirable that the casein to be produced for glue should be uniform in physical qualities. Although the exact significance of the borax solubility test for certain of the aspects of glue making is not clear, the improvement of this test as reported by Dr. Zoller furnished a method by which it was shown that grain-curd casein can be produced with certain very uniform physical characteristics.

The actual glue-making properties of grain-curd casein was not extensively studied. The signing of the armistice and the cancelling of the government contract for a test lot of 70,000 lbs. prevented any but small quantities of grain-curd casein from receiving glue-making tests. We are, however, indebted to the Forest Products Laboratory for the following report:

> We have not tested a sufficient number of these caseins, nor has the testing been sufficiently conclusive with respect to their merit for use in casein glues. The first glues which we made were based on formulas which were found to be effective for commercial caseins. The glues which were thus obtained were found to lack in waterproofing qualities, although the strength properties were very high. This led us to believe that the much greater purity of these caseins would require a change in the formula, which was effected practically by increasing the lime content. This is a logical conclusion when one considers the low ash, fat, and acidity, and the very high nitrogen content of these caseins. Working with a higher lime content in the glue formulas, we were able to produce very strong glues which satisfactorily resisted the boiling and soaking tests. They also showed very satisfactory results when tested immediately after coming from the soaking bath, thus indicating a high strength at high moisture content.

STUDIES ON TECHNICAL CASEIN. II—GRAIN-CURD CASEIN[1]

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Casein is an amphoteric electrolyte whose isoelectric point has been shown by Michaelis and Pechstein[2] to lie at H$^+$-ion concentration of 2.5×10^{-5} *N*. In terms of Sorensen's scale this is pH = 4.6. In other words, casein in dilute solution and under the conditions with which these authors worked acts chiefly as an acid in neutralizing bases at H$^+$-ion concentrations lower than 2.5×10^{-5} (pH values higher than pH 4.6), and as a base on the other side of this point. While it is doubtless true that in salt solutions, even of the concentrations found in milk, a simple consideration of the equilibria of casein ions at the isoelectric point in dilute "buffer" solutions is inadequate for many scientific purposes, it seems reasonable to suppose that at or near pH 4.6 we shall have not only maximum precipitation of the casein from milk, but also the maximum precipitation of casein *as casein*, uncontaminated with its compounds, except so far as these are carried down by occlusion and adsorption.

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[1] *J. Biol. Chem.*, **35** (1918), 127.

[1] Published by permission of the Secretary of Agriculture.

[2] *Biochem. Z.*, **47** (1912), 260

Since it was out of the question to expect a factory installation of a hydrogen electrode for the determination of the attainment of the proper pH, we fell back upon the use of the indicator methyl red, though fully conscious that methyl red does not conduct itself well in whey. It was found that when hydrochloric acid was added to milk until methyl red, added to the expressed whey, indicated pH, 4.6 the curd was of a remarkable consistence. Adjustment of the temperature of the milk to 34° C. and moderately rapid addition of the acid in about normal concentration gave a fairly uniform grain to the curd. The resilient mass of curd permitted extensive washing without the packing that ordinarily occurs. It held a porous texture under the pressure of the hand or of large quantities of curd, and permitted indefinite washing, provided the water was held at a H^+-ion concentration that was in equilibrium with the casein. In other words, having thrown down casein at a pH with which neutral casein is in equilibrium, it was necessary to maintain this equilibrium during the washing.

Many natural waters contain such small amounts of "buffer" salts that adjustment of their pH to 4.6 on a laboratory scale is a matter of extreme delicacy, but when the quantity of water is of the order of 5000 lbs., fairly accurate adjustment may be made by the addition of acid as strong as normal and with an indicator such as methyl red. With water so adjusted the curd has been washed on a semicommercial scale as many as nineteen times without any marked change in its texture. With water over-acidified there is danger of the formation of a gelatinous layer over the curd particles. This makes the curd grains stick together and in extreme cases may even transform the whole mass to a jelly. With unadjusted water containing alkaline salts there is a tendency to redispersion of the casein and the loss of resiliency of the curd particles, and consequently of the porosity of the mass, upon which efficient commercial washing depends.

It will therefore be seen that one of the chief points to be observed is the control of the H^+-ion concentration during both precipitation and washing. As mentioned before, it was known from the work of Clark and Lubs[1] that methyl red does not give in whey indications of pH that agree with hydrogen-electrode measurements. A more systematic study of the colorimetric and the electrometric indications reveals the relations plotted in Fig. 1. Inspection of these curves shows that, when methyl red indicates pH 4.6 by comparison with a standard pH 4.6 buffer solution, the true reaction is pH 4.1. Now it so happens that at or near pH 4.1 the casein curd takes on that peculiar resiliency so valuable for commercial washing and handling. Thus more or less by accident there was obtained the favorable condition, and consequently the use of methyl red and the specification that acid should be added till the whey attained an *apparent* pH of 4.6 was insisted upon.

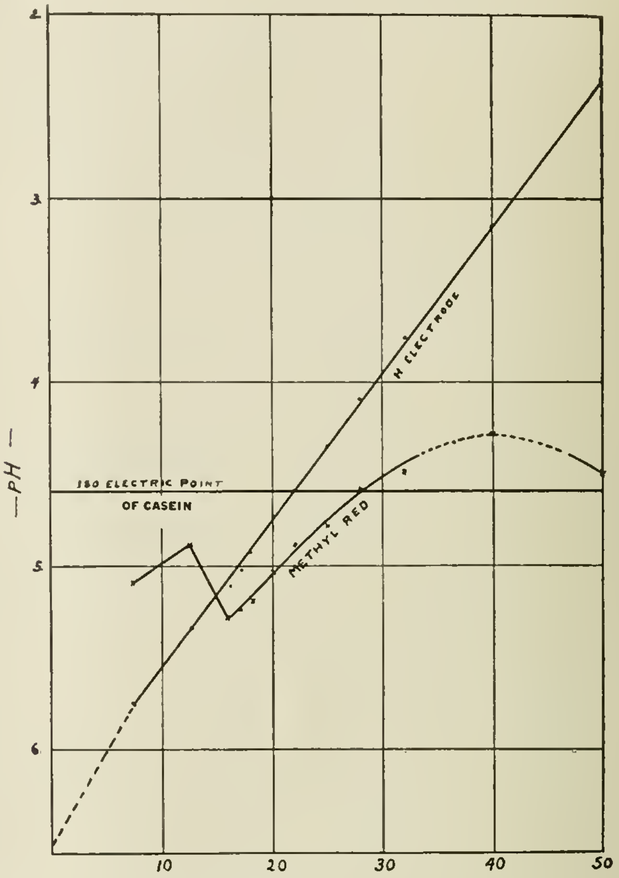

Fig. 1—Electrometric and Colorimetric Titration Curve of Fresh Skim Milk

Under commercial conditions of manufacture the time factor is important. Complete equilibrium between acid and milk constituents is not attained within the ordinary time of operation. This is shown by the reversion of the reaction of whey toward higher pH values as curd and whey are left in contact. Therefore the tendency will be toward more rapid elimination of the basic constituents on acidification to such point as that which experience shows is favorable for texture.

It will also be seen in Fig. 1 that methyl red ceases to show well the differences in pH when the whey is acidified much beyond the required point. Caution is therefore necessary when the proper precipitating point is reached.

In the adjustment of the wash water, methyl red probably indicates quite closely the true pH. Experience has shown that the wash water should be adjusted to 4.8, and methyl red indicates this point very well.

In applying this method of control, standard buffer solutions[1] were provided, and the workmen were instructed to acidify the milk with hydrochloric acid until a test tube half filled with clear whey and five drops of 0.04 per cent methyl red solution matched in color a like quantity of standard pH 4.6 containing 5 drops of the indicator.

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[1] *J. Bact.*, **2** (1917), 1, 109, 191.

It will be noted that this imposed upon the workman only a more careful color comparison of the kind to which he had become accustomed in the ordinary titration of milk with phenolphthalein. At the same time it relieved him of the preparation and care of standard alkali solutions and all the paraphernalia of titration. Workmen readily caught on to the new method and were not troubled by the scientific nomenclature of pH. It is obvious of course that, ultimately, dependence is placed upon the correct preparation of the standard buffer solutions. Once prepared, they provide a vision which memory can retain over periods when the standards are not available, but it is best to have recourse to accurately prepared standards.

By control of the acidity at all points of the procedure, and by controlling the size of the curd grains through adjustment of temperature and rate of addition of acid, the casein was thrown down and carried through subsequent operations in the form of more or less uniformly sized grains whose physical properties determined the commercial applicability of the procedure. It therefore seemed appropriate to call this type of technical casein "grain-curd casein." As such it was described. The following brief instructions issued to manufacturers summarize the procedure.

INSTRUCTIONS FOR THE PREPARATION OF TECHNICAL GRAIN-CURD CASEIN

The skim milk should be as free from fat as possible and as sweet as possible. It should be delivered to the casein precipitating vat at a temperature of 90° F. or, preferably, lower.

The hydrochloric (muriatic) acid used in the precipitation of the casein should be diluted with water in the ratio of 1 lb. of acid (20° Bé.) to 8 lbs. of water.

The wash water used in washing the casein should be made up as follows: To a tank of water add hydrochloric acid until an acidity of 4.8 is shown by use of the methyl red indicator solution. Stir the acid thoroughly into the water.

The indicator solution may be prepared by dissolving 0.4 g. of the pure crystals of methyl red in 1000 cc. of 95 per cent grain alcohol. This gives about 0.04 per cent solution.

The indicator standards should be prepared by measuring, with a 10-cc. pipet, 10 cc. of the standard solution mixtures marked "4.6–4.8," etc., into test tubes of uniform diameter, and adding to each 10-cc. portion 5 drops of the methyl red indicator. Close each test tube with a clean cork stopper and seal with paraffin. If it is found necessary to use 10 drops of the indicator solution in the unknown solution in order to make easier readings, this may be done. In any case, the same number of drops should be used in the "unknown solution" as are used in the indicator standard.

PROCEDURE IN THE PRECIPITATION OF CASEIN—(1) Heat the skim milk, if reasonably fresh, to 94° F. If the milk is very sour, a temperature of 93° F. is more satisfactory. Under no circumstance should the temperature be above 96° F.

(2) Add the diluted hydrochloric acid to the milk in fine spray and stir rapidly until the the milk "breaks." Just before the milk breaks the acid should be added more slowly, but the stirring should be rapid. It is good economy to add no more acid *at this stage* than is required for the complete separation of the casein from the whey, but it is essential that the casein, after having had most of the whey drained away, should be acidified as in Paragraph 4.

(3) Allow the curd to settle in the vat; pull it away from the gate valve and drain off through the drain cloth at least one-half of the whey as indicated by a measuring stick.

(4) Stir the curd thoroughly but not rapidly with the remaining whey in order to break up any clumps, so that the washing may be done more thoroughly. Now add more acid in small quantities, mixing it with the curd. Test 10-cc. portions of the whey by means of the indicator solution until an apparent acidity of pH 4.8 to 4.6 is obtained. It is well to avoid breaking the curd into fine particles at this stage, so that the drain cloth will not become clogged. The curd should be firm but not slippery when the correct quantity of acid has been added. The temperature has a marked influence on the "feel" of the curd at this stage.

(5) Now drain off the remainder of the whey through the drain cloth, retaining as much of the curd in the vat as practicable.

(6) Pour a little wash water[1] over the casein which has run upon the drain cloth. Also wash the casein in the vat by completely covering with wash water and mixing the curd carefully with it.

(7) Now drain all curd upon the drain cloth and wash again by pouring a liberal quantity of wash water over it. Allow the casein to drain as well as practicable before placing it in the press.

(8) Dump the casein and fill it into the casein press in thin layers so that the pressed cake is about 2.5 in. in thickness. At first very little pressure should be brought to bear upon the casein in the press. The pressure may be increased slowly as the liquid drains from the cake. Uniform pressure should be maintained over the entire cake.

(9) The pressed casein should now be ground through a curd mill and spread in layers about 0.25 in. thick on trays in the drying tunnel.

(10) The temperature of the drying tunnel should be about 125° F., using a strong blast of air.

The drain racks used in the commercial operation of the method were open-bottom. For semicommercial studies we used a closed-bottom vat with gate. The drain cloth was suspended in this by a cradle of coarse wire netting. With this arrangement the curd could be kept immersed in the wash water as long as desired. The drain cloth found to be especially suited for casein was a coarse-threaded, fine-weave marquiset.

Since the preparation of the standard solutions requires the accuracy of a well-equipped laboratory, they will not be described here. A detailed description will be found in the paper by Clark and Lubs. During the war the standards were supplied by this Division. They can now be obtained from supply houses.

In making the colorimetric comparisons a so-called comparator will be found useful. This consists of a block of wood with four or six holes bored in pairs, parallel to one another, to hold the test tubes, and with smaller holes bored perpendicular to the others, through which the test tubes are viewed. The comparison is made between a pair of tubes consisting of the whey plus indicator backed by a water blank, and a pair consisting of the colored standard backed by an uncolored tube of whey.

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[1] Clark and Lubs, *Loc. cit.*

[1] It must be remembered that this wash water is the very dilute HCl solution described above.

Table I—Analysis of Typical Grain-Curd Caseins Prepared in the Dairy Division Laboratories on a Semicommercial Scale[1]

Laboratory No.	Condition of Milk	Moisture Per cent	Ash Per cent
A-120	Old skim milk	7.7	1.43
A-121	Sour skim milk	6.25	1.36
A-123	Fresh skim milk	5.52	1.55
A-129	Fresh skim milk	7.93	1.90
A-125	High-acid milk	7.32	1.79
A-130	Fresh milk	5.43	1.83
A-135	Fresh milk	7.44	1.57
A-137	Fresh whole milk	8.94	1.85
A-147	Fresh skim milk	5.03	2.03
A-148	Fresh skim milk	5.81	2.03

[1] These caseins were all well washed.

In Table I are shown the ash analyses of typical grain-curd caseins manufactured on a semicommercial scale in the creamery of the Dairy Division laboratories. When the process was brought to large-scale manufacture it was found that the handling of 50,000 to 80,000 lbs. of milk a day precluded the amount of washing which had been considered feasible in the semicommercial tests. The casein could not receive more than two washings with adjusted wash water, the washing usually being accomplished while the casein was in the drain rack. Consequently, the commercial samples from six different factories, typical analyses of which are listed in Table II, show a higher ash content.

Table II—Analyses of Grain-Curd Caseins Manufactured on a Commercial Scale in Large Factories[1]

Factory	Moisture Per cent	Ash Per cent	Fat Per cent
A	7.37	2.55	0.15
B	7.54	2.78	0.24
C	7.41	2.86	0.21
D	7.13	2.90	0.08
E	8.34	1.90	0.11
F	8.73	2.10	0.11

[1] The authors desire to thank Prof. E. J. Lea, of the California State Bureau of Foods and Drugs, for his generous aid in the analytical control of the first casein manufactured on a large commercial scale by the grain-curd process.

INFLUENCE OF WASHING UPON THE ASH CONTENT OF CASEINS MADE BY THE GRAIN-CURD PROCESS

When grain curd is subjected to discontinuous washing with adjusted water it is possible to remove practically all the soluble salts. Experiments in this laboratory showed that with careful precipitation and careful washing by decantation the ash content could be reduced to 0.6 per cent.[1] This is possible only under ideal conditions. The curve in Fig. 2 illustrates the average effect of continued washing on a semicommercial scale. Point zero on the abscissa refers to the unwashed casein pressed free from whey, dried, and analyzed for moisture and ash. The washing was accomplished by suspending the drained curd in water adjusted to pH 4.6, and allowing it to remain under the water for a period of 15 min. with frequent stirring. It was then drained from the water, a portion dried and analyzed, and the remainder again suspended in fresh water as above. The ash content is expressed in per cent calculated to moisture-free casein.

Where large vats of skim milk are treated at one time the curd grains are much larger and the massiveness of the curd makes efficient washing impossible with the ordinary drain-rack method. A glance at Table II shows that the ash content of these commercial caseins is remarkably constant when only two washings were conducted. The total ash content is well within the limit set by the Office of Aircraft Production for casein which was to be used for airplane glue. While a lower-ash casein may not be necessary for the chief industrial uses to which casein is put, it is possible to lower the ash content by more efficient washing.

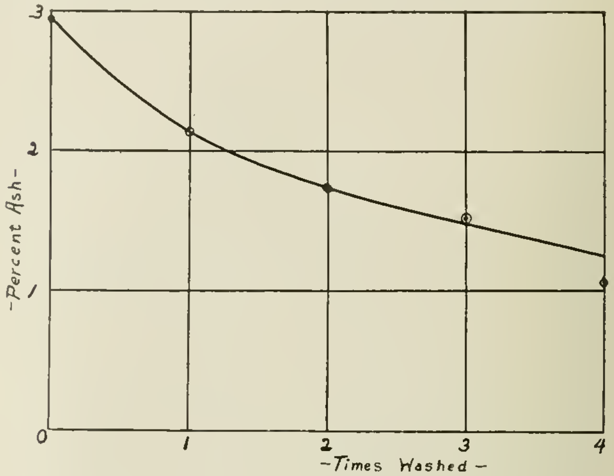

Fig. 2—Influence of Washing on Ash Content of Grain-Curd Casein

HYGROSCOPICITY OF COMMERCIAL CASEINS

Since government specifications required a minimum moisture content it was of some importance to determine by laboratory tests the probabilities of change in moisture content between creamery and glue factory.

Eight different caseins, two each of cooked-curd, natural-sour, grain-curd, and sulfuric, were taken from stocks on hand and were screened successively through a 20- and 30-mesh sieve. The casein retained by the 30-mesh sieve was used in the experiment. The samples were carefully analyzed for moisture, ash, and fat. Two-gram portions were accurately weighed into wide, flat-bottomed, glass-stoppered weighing bottles with full vertical sides. These were then placed in the humidor, which was in turn set in an air bath controlled to within 0.5° C.

The humidor consisted of a large desiccator, the bottom of which contained a 2.0 cm. layer of a solution of known vapor pressure. These solutions were prepared in each instance from pure sulfuric acid, and the concentrations used were those corresponding to the published vapor pressures[1] expressed in milimeters of mercury. The caseins were suspended in the atmosphere above the liquid with the stoppers completely removed from the bottles.

The conduct of the casein in six different sets of vapor pressures was studied. The caseins were removed from the humidor, covered quickly, and immediately weighed; they were then returned to the humidor without undue exposure. They were not allowed to reach a constant weight in every instance. Two separate experiments were conducted; in either case four caseins representing the four different types were employed.

Instead of presenting data for both experiments, complete data from one experiment are given, since it is representative of the hygroscopic tendencies in all the caseins studied in these and other experiments.

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[1] As determined by the method called for by the Office of Aircraft Production.

[1] Regnault's Table, Landolt, Börnstein and Roth, "Physikalisch-Chemische Tabellen," p. 426 (4th Ed.).

TABLE III—ANALYSES OF TYPICAL CASEINS

LABORATORY NO.	CASEIN	MOISTURE Per cent	ASH Per cent	FAT Per cent
56.103B	Cooked curd	8.56	6.03	0.08
56.136	Sulfuric	8.00	4.12	0.33
D 11	Natural-sour	7.14	3.45	0.24
Z 20	Grain curd	7.41	2.96	0.21

In Table III will be found analytical data bearing upon the caseins studied. Table IV gives the conditions and results of the hygroscopic measurements. Columns 4, 5, 6, and 7 show the amount of moisture in milligrams lost or gained by the casein (calculated to one gram weight of moisture, ash, and fat-free casein) during the intervals of exposure to the different humidities. It may be mentioned, however, that no correction was made for the possible traces of milk sugar in the casein, for it is believed that this would not affect the relative importance of the results.

TABLE IV—MOISTURE GAIN OR LOSS OF TYPICAL CASEINS

Vapor Pressure Mm. Hg	Temperature ° C.	Time of Exposure Hrs.	MOISTURE GAINED (G) OR LOST (L) 56.103B Mg.	56.136 Mg.	D 11 Mg.	Z 20 Mg.
10.0	+20	12	(G) 29.6	(G) 25.4	(G) 23.2	(G) 16.3
....	..	18	33.5	31.3	29.0	22.9
....	..	24	33.4	31.7	29.8	26.2
1.0	—10	12	(L) 46.4	(L) 54.8	(L) 56.6	(L) 23.1
....	..	24	56.5	60.4	59.8	39.2
18.5	+30	6	(G) 53.3	(G) 46.7	(G) 42.2	(G) 22.8
....	..	18	64.6	59.3	56.3	37.2
....	..	24	64.2	61.2	57.5	40.5
28.0	+30	6	126.4	100.5	93.3	58.4
....	..	18	154.1	122.7	112.0	80.3

In Fig. 3 the hygroscopicity curves of caseins 56.103B and Z 20 are reproduced from data obtained from the tables above. An inspection of the table shows that these two caseins represent the two extremes in hygroscopic tendencies, the other two falling between. This divergence in the moisture-absorbing tendency is characteristic of these two types of casein and was borne out in all the studies directed toward this question.

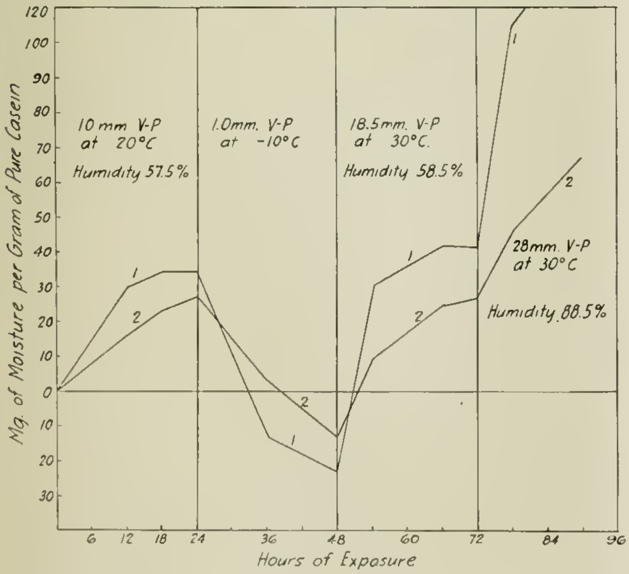

FIG. 3—HYGROSCOPICITY CURVES OF COMMERCIAL CASEINS
1 = GRAIN CURD, 2 = COOKED CURD

Further inspection of the curves and tables gives evidence that, although we start with a moisture content indicated in the analytical data, the caseins change weight with great rapidity when subjected to atmospheres only slightly different from the normal. In cool, dry air they rapidly lose weight, while in warm, moist air the gain in weight is fast. At humidities between 85 and 95 per cent the absorption of moisture becomes so great that we are justified in terming this zone "dangerous" for the casein. The humidity corresponding to a vapor pressure of 28 mm. at 30° C., as used in one of the experimental sets reported in Table II, is about 89 per cent. This shows that casein 56.103B has increased in weight by about 10 per cent in being subjected to this humidity for a short interval of time. The other caseins show increases from 6 to 9 per cent. In one set, not included in the tables presented, where the humidity was regulated to 98 per cent, the average increase in weight of the four caseins studied was 21.2 per cent. These increases in weight are all increases above the content of moisture already in the samples.

Aside from the idea of total gain or loss of weight by caseins under different atmospheric conditions, two things are very strikingly brought out by this study. Cooked-curd casein (or casein that has resulted from high-temperature treatment) is noticeably more sensitive to changes in humidity than any of the other three types studied; and in most cases it not only shows a greater avidity for moisture, but also tends to hold it more firmly. The second feature worthy of consideration is the conduct of grain-curd casein toward different humidities. In every instance grain-curd casein responds slowly to changes in atmospheric conditions and it tends to hold a smaller quantity of moisture.

At first glance it may be thought that this is traceable to the salt content. And while this may be the cause of the slow rate in the case of grain curd, it does not hold good without exception in case of cooked curd. The commercial sulfuric casein contains as much ash as cooked curd, or more, yet it behaves entirely differently. The natural-sour also contains considerable ash, but it parallels the conduct of the sulfuric. A more logical reason for the phenomenal conduct of cooked curd is believed to exist in the effect of heat upon the casein molecule.

SUMMARY

To meet the demand for the high grade of commercial casein required for the manufacture of glue to be used in the construction of aircraft, a controlled method of manufacture was devised and put into large-scale operation.

This method was based primarily upon the properties of casein as an amphoteric electrolyte, the chief control being exercised through adjustment of the H^+-ion concentration at which the casein is precipitated and at which the casein is washed.

The casein so produced met the analytical requirements of the government specifications, gave promise of being suitable for the manufacture of high-grade glue, and possessed uniformity in physical characteristics which would doubtless have eliminated the necessity for troublesome changes in glue formulas.

An outline of the theoretical aspects, details of manufacture, and studies of the effect of washing and of exposure to atmospheres of different moisture content is reported.

STUDIES ON TECHNICAL CASEIN. III—METHODS OF ANALYSIS[1]

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Received June 28, 1920

The Forest Products Laboratory, which was charged with the supervision of the manufacture of glue from casein, issued a set of methods covering the testing of casein. These methods embodied the best information available at the time and were officially adopted by the Office of Aircraft Production. It was soon found, however, that in some cases wide discrepancies arose among the results of different analysts, and it therefore became a matter of vital importance to study analytical methods in order that the extent to which grain-curd casein met the specifications might be determined with greater certainty.

As methods of analysis have since been extensively reported from the Forest Products Laboratory,[2] only a brief summary of our experience will be given.

MOISTURE

The tentative method upon which the specification was based called for drying a 3-g. sample of casein for 5 hrs. at 98° C. An electric oven was first used, but it was impossible to maintain all parts of the oven at the same temperature, and unless the dishes were placed side by side the checks did not agree. Better results were obtained in a large double-walled water oven. The temperature around the center remained quite constant, about 98° C., and very satisfactory checks were obtained.

As a part of the regular routine in the determination of fat by the ether-extraction method, the Bureau of Chemistry determined the moisture in 79 samples of casein submitted by us. These determinations were made by drying to constant weight in partial vacuum at the boiling point of water. Moisture determinations were also made on the same samples by the tentative method mentioned above, using the double-walled water oven. Space does not permit the publishing of these figures in detail. The average per cent of moisture for 79 samples, as determined in the open dish at 98° C., was 7.44. The corresponding per cent determined by the partial-vacuum method was 8.21, showing a difference of 0.77 per cent in favor of the latter method.

In connection with the ash method, it was thought desirable to see how closely several different analysts would agree when following the tentative method independently. Five samples of casein, representing rather a wide range, were placed in wide-mouthed, glass-stoppered bottles, and submitted to five analysts. In four cases the analysts were allowed to take their own subsamples from the bottles. The per cents of moisture obtained by the different analysts are given in Table I.

A study of the figures reveals some interesting points. In the case of Sample 1, one of the analysts would have passed it, 8 per cent water being allowed as the maximum, while the other four would have rejected it. The range is from 7.55 to 9.01 per cent, or a difference of 1.46 per cent between the highest and lowest figures. In Sample 2, the range is from 7.80 to 9.34 per cent. This sample would also have been passed by one analyst and rejected by the others. Substantially the same discrepancies are found in the other cases.

Table I—Results on Moisture Obtained by Different Analysts

Analyst	Sample 1 Per cent	Sample 2 Per cent	Sample 3 Per cent	Sample 4 Per cent	Sample 5 Per cent
1	8.96	9.34	9.16	8.44	8.15
2	8.75	8.79	7.74	8.00	7.55
3	7.55	7.80	7.80	6.99	7.48
4	9.01	8.80	8.42	7.89	8.05
5	8.63	8.42	8.16	7.77	7.87

It requires no further discussion to show that a method yielding such widely different figures in the hands of different analysts will not meet the requirements. It is also evident that the open-dish method yields results that are too low. For reliable results in moisture the standard method of drying to a constant weight in partial vacuum at the boiling point of water should be used.

ASH

The tentative method for ash, in the hands of different analysts, yielded discrepancies even greater than in the case of the moisture. These discrepancies, however, were limited largely to low-ash caseins.

This is well illustrated in Table II, which gives the results of the determination of ash by five analysts who included this work with the moisture determination discussed in a preceding paragraph.

Table II—Results on Ash Obtained by Different Analysts

Analyst	Sample 1 Per cent	Sample 2 Per cent	Sample 3 Per cent	Sample 4 Per cent	Sample 5 Per cent
1	1.70	3.46	4.66	4.05	3.31
2	1.90	3.61	4.74	4.12	3.68
3	1.20	3.20	4.53	3.48	3.35
4	1.14	3.14	4.37	3.67	3.37
5	1.53	3.36	4.38	3.58	3.43
Average	1.49	3.39	4.54	3.78	3.43

Sample 1 is a low-ash casein, the others are medium and high. Considering the average figure for each sample as being the correct figure, it is found in Sample 1 that the individual determinations vary as much as 27 per cent from that figure, while in the others the largest variation is but 9 per cent.

In endeavoring to explain the discrepancies in the ash determination on low-ash casein, the thought at once occurred that there was too little base present to hold back the organic phosphorus, and that in consequence the phosphorus not fixed was volatilized to a small or large extent, depending on the temperature and length of time of ignition.

To find whether this was the case, a solution of calcium acetate was prepared by dissolving calcium carbonate in acetic acid according to the methods of the A. O. A. C.[1] Three grams of the casein were weighed into a quartz dish and 5 cc. of the calcium acetate solution added. Two different solutions were used, one yielding 0.0761 g. CaO and the other 0.1523 g. CaO per 5 cc. on ignition. The dishes were allowed to stand several minutes until the solution was absorbed, then dried in a drying oven, carefully charred over a small flame, and finally ignited in an electric muffle furnace maintained at low redness until a white or nearly white ash was obtained. The amount of CaO introduced by the calcium acetate solution was subtracted from the weight of the ash. Early in the work, until quartz dishes were obtainable, porcelain dishes were used. It was noted that the glazing on these dishes soon became roughened, and it seemed possible that a base might be supplied to the phosphorus by the glazing. To prove this point, determinations were run in both quartz and porcelain dishes.

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[1] Published by permission of the Secretary of Agriculture.

[2] F. L. Browne, This Journal, **11** (1919), 1019.

[1] Association of Official Agricultural Chemists, "Official and Provisional Methods of Analysis," **1908**; U. S. Dept. of Agriculture, Bureau of Chemistry, *Bulletin* **107** (revised), 21.

The results are included with those from the added base experiment in Table III. The phosphorus was determined in the ash as follows: The ash was dissolved in 5 to 10 cc. of concentrated nitric acid on the steam bath; washed into a small beaker, and boiled to oxidize the phosphorus; neutralized with ammonia; made faintly acid with nitric acid; and the determination completed in the usual manner, using ammonium molybdate and magnesia mixture.

TABLE III—EFFECT OF ADDED CALCIUM ACETATE ON THE DETERMINATION OF ASH CONSTITUENTS

METHOD	Low-Ash Casein Per cent	Medium-Ash Casein Per cent	Medium-Ash Casein Per cent	High-Ash Casein Per cent
Ash, untreated sample, porcelain dish	1.51	2.41	3.09	4.13
Ash, untreated sample, quartz dish	1.68	2.45	3.22	4.20
Ash, 5 cc. $Ca(C_2H_3O_2)_2$ solution (0.1523 g. CaO added)	2.25	2.66	3.23	4.60
Ash, 5 cc. $Ca(C_2H_3O_2)_2$ solution (0.0761 g. CaO added)	2.23	2.54	3.26	4.52
P, untreated sample	0.51	0.77	0.74	1.05
P, 5 cc. $Ca(C_2H_3O_2)_2$ solution (0.1523 g. CaO added)	0.80	0.80	0.88	1.04
P, 5 cc. $Ca(C_2H_3O_2)_2$ solution (0.0761 g. CaO added)	0.80	0.80	0.89	1.04

It will be noted that about 25 per cent more ash was obtained in the case of the low-ash casein when a base was added than was obtained by plain ignition; also that this ash contained about 35 per cent more phosphorus than did the ash from the untreated casein. This is not true of the medium- and high-ash caseins, which of course would follow on the assumption that these caseins contained sufficient calcium. Calcium determinations were made on two of these samples by the method described in another paragraph. The low-ash casein contained 0.28 per cent CaO, while the high-ash casein contained 1.68 per cent CaO.

These results indicate that an added base is necessary in low-ash caseins if accurate results are desired. It is not necessary in medium- or high-ash caseins.

There seems to be little, if any, difference in the results obtained in porcelain and quartz dishes. Those made of quartz are in every way preferable, however. Quartz evaporating dishes 2 in. in diameter are a convenient size; the porcelain dish will not stand more than a few ignitions before cracking.

The best results in ash work are obtained by first heating over a very low flame and taking care that the contents of the dishes do not burst into flame. This operation should take about an hour. After the casein has become thoroughly charred, the dishes are placed in a muffle furnace (preferably electric) and the ignition completed at as low temperature as is consistent with obtaining a white or nearly white ash.

FAT

According to the tentative methods of the Forest Products Laboratory, this determination is made by extracting with ether in the usual way in a continuous extractor. The method is time-consuming, and in an effort to reduce this time the Roese-Gottlieb method was modified to apply to casein, as follows: Weigh out a 1-g. charge of the casein into the Roehrig tube, and add 10 cc. of water. Shake vigorously, but not so as to carry particles of casein near the top of the tube. Let soak for at least 15 min.; a longer time is advisable if the sample is not finely ground. Add 2 cc. of strong ammonia water, and shake vigorously, again taking care not to carry particles of casein near the top of the tube. Let stand 10 min. with occasional shaking. Add 10 cc. of 95 per cent alcohol and shake until the casein is completely dissolved. From this point proceed as usual with the Roese-Gottlieb method.

The signing of the armistice made the work on casein less pressing, and this phase of the work was not carried so far as might be desired. Table IV gives the results on fat in casein both by the ether-extraction method and by the modified Roese-Gottlieb method. The determinations by the ether-extraction method were made by the Bureau of Chemistry.

TABLE IV—COMPARATIVE FIGURES FOR FAT OBTAINED BY THE ETHER-EXTRACTION METHOD AND THE MODIFIED ROESE-GOTTLIEB METHOD

SAMPLE	Fat by the Ether-Extraction Method Per cent	Fat by the Modified Roese-Gottlieb Method Per cent
Grain-curd casein	0.08	1.50
H_2SO_4 cooked-curd casein	0.20	2.35
Buttermilk casein	3.79	3.92

It will be noted that the results by the Roese-Gottlieb method are higher than those obtained by the regular extraction method. Two explanations naturally suggest themselves: (1) The ether-extraction method does not remove all the fat; and (2) the extract in the Roese-Gottlieb method contains other material than fat. We believe the first explanation is the true one. The grains of casein are hard and not easily penetrated by the solvent. This is shown very well in a later table giving the results on sugar extracted with 50 per cent alcohol from casein of different sized granules. In the modified Roese-Gottlieb method the casein goes into solution, and it is impossible for any fat to remain locked up in the casein granules. More work is needed along this line, but there is certainly good evidence for believing that the ether-extraction method fails to remove all the fat, except perhaps when the casein is ground to impalpable powder.

SUGAR

Sugar in casein was determined by adapting the method for determining sugar in cattle food. Ten grams of the casein were weighed into a 500-cc., wide-mouthed bottle, and 250 cc. of 50 per cent alcohol added. The bottle was shaken for 4 hrs. in a motor-driven shaking machine, then allowed to stand for several hours, and the solution decanted. This solution was then centrifuged, although this step may not have been absolutely necessary. One hundred cc. more or less, according to the quantity of sugar present, of this nearly transparent solution were taken for the determination, which from this point was conducted according to the method of Bryan, Given, and Straughn.[1] Results are given in Table V.

TABLE V—SHOWING PER CENT OF SUGAR IN SAMPLES ANALYZED[1]

SAMPLE	SUGAR Per cent
Natural-sour casein	Trace
H_2SO_4 cooked-curd casein	1.13
Grain-curd buttermilk casein	0.95
H_2SO_4 cooked-curd buttermilk casein	0.62
H_2SO_4 uncooked-curd buttermilk casein	0.33
Grain-curd casein, not washed	3.96
Grain-curd casein, washed well	1.43
Grain-curd casein from partly sour skim milk, not washed	5.43
Grain-curd casein from partly sour skim milk, washed well	0.56

[1] For description of various manufacturing types of casein see bulletin cited. The so-called grain-curd casein listed in this and other tables was made according to a process developed by the Dairy Division, described in Part II of this series.

Arnold O. Dahlberg, "The Manufacture of Casein from Buttermilk or Skim Milk," U. S. Dept. of Agriculture, *Bulletin* **661** (1918).

In the sugar determination the identity of the casein granule is not lost, and in order to learn whether the size of the granule has an influence on the quantity of sugar extracted by the 50 per cent alcohol, two samples of casein were separated by means of sieves into lots of different-sized granules. Table VI gives the per cents of sugar obtained on the different lots.

TABLE VI—EFFECT OF SIZE OF GRANULES ON DETERMINATION OF SUGAR

Sample	Original Sample Per cent	Less than 100 Mesh Per cent	40 and 100 Mesh Per cent	20 and 40 Mesh Per cent	Over 20 Mesh Per cent
1	0.56	0.90	0.65	0.57	0.50
2	2.09	3.09	2.01	1.53	....

PHOSPHORUS AND CALCIUM

Reference has already been made to the determination of phosphorus and the method given that was used in its determination in the ash. Several methods were tried for determining the phosphorus in casein without ashing it, among them being digestion with aqua regia. This method gave low results. The method which was finally adopted, and which gave very satisfactory results, was the official method for determining total phosphorus in fertilizers, using Method (*a*) 2 for oxidizing and getting the casein into solution.[2] It was not found necessary to evaporate after adding the magnesium nitrate solution, since by careful manipulation the mixture could be dried and ignited over a Bunsen burner in one operation.

TABLE VII—PER CENT OF CALCIUM OXIDE AND PHOSPHORUS IN ASH

DESCRIPTION OF SAMPLE	CaO			PHOSPHORUS		
	Ash Per cent	Aqua Regia Per cent	In Ash Per cent	In Ash Per cent	Aqua Regia Per cent	Magnesium Nitrate Per cent
Argentine casein	3.68	0.90	0.94	1.08	0.95	1.16
Natural-sour casein	2.63	0.54	0.53	0.85	0.73	1.00
H_2SO_4 cooked-curd casein	4.41	1.59	1.76	1.18	1.04	1.09
H_2SO_4 uncooked-curd casein	5.21	1.96	....	1.08	1.08	1.25
Grain-curd casein, excessively washed	0.38	none	none	0.22	0.76	0.87
HCl cooked-curd casein	5.95	2.50	2.43	1.37	0.94	1.34
Grain-curd casein, made in Dairy Division	1.57	0.24	0.32	0.59	0.77	0.89
Grain-curd casein, made in factory	3.63	1.26	1.12	....	....	1.03
Ejector buttermilk casein	1.27	0.12	0.08	....	....	0.79

The determination of calcium offers no difficulty, since all of it is found in the ash after ignition. It can be determined also by digesting the casein with aqua regia. The customary procedure of precipitating with ammonium oxalate and igniting to calcium oxide was followed.

Table VII gives the results of the determination of phosphorus and calcium in the samples of casein analyzed. The figures are all based on the moisture-free condition.

Attention may again be called to the behavior of the low-ash casein when ignited. In the case of the grain-curd casein which was excessively washed, there was no calcium found in the ash. The true per cent of phosphorus as found by treatment with magnesium nitrate was 0.87, while that found in the ash was but 0.22, showing that nearly 75 per cent of the phosphorus was lost while ashing, since there was no calcium present to combine with it. In the case of the grain-curd casein made in the Dairy Division, which has a low calcium content, the true per cent of phosphorus was 0.89, while that remaining in the ash was but 0.50 per cent.

ACKNOWLEDGMENT

The author wishes to make acknowledgment to Messrs. F. C. Lamb and A. Biddle who were detailed by the Bureau of Aircraft Production to assist in the analytical work.

SUPPLEMENTARY NOTE ON THE "FREE ACIDITY" OF TECHNICAL CASEIN

By W. M. Clark

The Office of Aircraft Production specified that all casein to enter into glue for aircraft should have not more than a certain quantity of "free acid." The fact that grain-curd casein was to be washed with acidified water seemed to defy the intention of the specifications and caused some surprise. It may be well, therefore, to add a word of explanation.

Theoretically at least, casein when precipitated at its isoelectric point should consist chiefly though not wholly of free casein uncombined with acid or alkali. The isoelectric point represents only a minimum for *both* alkali and acid caseinates, so that there must remain some of each which would doubtless be carried down together with some of the milk salts. In the grain-curd process, however, the isoelectric point is somewhat overstepped, so that a little acid caseinate may be produced. This, however, tends to release the casein from its basic combinations. As mentioned before, complete equilibrium is not attained, but the tendency is in the desired direction. Now, on washing with water held just a trifle on the alkaline side of the isoelectric point, there is a continuation of the environment which alone is conducive to the separation of pure casein. At that reaction the strong acid, hydrochloric, can exist "free" only to a very minute extent. If chlorides enter into the commercial product it is only because the washing has not been extensive.

Extensive washing would finally require only an indetectable quantity of acid, and at last when free casein alone was present its own acidity would bring the acidity of pure distilled water to the isoelectric point of pH 4.6.

Pure water would require only to be about 0.00001 *N* with hydrochloric acid to be at the isoelectric point of casein. This is an extreme case, but it represents the direction toward which the logic of the method points. To differentiate the chloride content due to the natural salts of the milk and that due to the absorbed acid added during the process of manufacture would be a difficult task. And to separate titrable acidity due to acidic salts from that due to absorbed acid is equally difficult.

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[1] "Extraction of Grains and Cattle Foods for the Determination of Sugars: A Comparison of the Alcohol and the Sodium Carbonate Digestions," U. S. Dept. of Agriculture, Bureau of Chemistry, *Circular* **71** (1911).

[2] Association of Official Agricultural Chemists, "Official and Provisional Methods of Analysis," **1908**; U. S. Dept. of Agriculture, Bureau of Chemistry, *Bulletin* **107** (revised), 2.

There remains, of course, the fact that a well-standardized titrimetric procedure will indicate differences of not very clear theoretical significance, but nevertheless capable of aiding the judgment. Such procedures indicate in a very rough way that careless handling of the curd by methods which offer no control over the acid used in precipitating and washing may result in the inclusion of considerable quantities of free acid.

On the other hand, the method for estimating the so-called free acidity which was included in the specifications was quite inadequate. It was directed that a given weight of casein be dissolved in an excess of alkali, and that the unneutralized acid be titrated with phenolphthalein as an indicator. When analyzed, this procedure consisted only in titrating to an arbitrary pH, as indicated by phenolphthalein, a mixture of amphoteric protein, occluded salts, and the products of alkali hydrolysis of the protein. As was to be expected, it gave no consistent results, partly because of the difficulty of titrating to an arbitrary and insignificant pH and partly because of the hydrolysis of the casein.

Some careful studies were made with the hydrogen electrode as indicator, and by extrapolating back to zero time of contact between alkali and casein it was found that a representative sample of grain-curd casein agreed very closely with the "free acid" in casein "nach Hammarsten." Unfortunately the details of these experiments were lost in a fire.

STUDIES ON TECHNICAL CASEIN. IV—STANDARDIZATION OF THE BORAX SOLUBILITY TEST FOR COMMERCIAL CASEINS[1]

By Harper F. Zoller

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Received June 28, 1920

The casein solubility test as conducted in general practice has been as follows: "To 50 g. of casein (ground to pass a 20-mesh sieve) are added 300 cc. of water containing 7.5 g. of borax. The mixture is stirred thoroughly and is immediately set in a water bath controlled at a temperature of 65° C. With continuous stirring the casein should be completely dissolved in 10 min." This test[2] is largely used to determine whether casein is suitable for the coating of paper.

The fact that a borax solution buffers the H^+-ion concentration in a zone (roughly from 9.0 to 10.0 pH) where there is scarcely any alkaline hydrolysis of casein suggests this as a valuable solvent in which caseins may be differentiated from the standpoint of physical constitution. From a study of the viscosity of a variety of caseins in borax solutions it was realized that there was no parallelism between the viscosity and the contents of ash or acid. Sutermeister[3] has since published results of a somewhat different nature, but materially confirms the above findings. From a more careful study of the viscosity of certain caseins the author finds that there is a correlation between the viscosity of caseins and certain physical properties (hydrophilic) which are a result of the heat treatment of the casein before or after separation from milk. Table I includes the observed viscosity of some commercial caseins in borax as solvent.

The 0.2 *M* borax solution at 30° C. was added to exactly 10 g. of each casein and thoroughly stirred. This was permitted to stand, with frequent stirring, for 30 min., when 75 cc. of distilled water at 30° were added to each mixture, and the mixture stirred until smooth. The solutions were then allowed to stand in a constant temperature water bath at 30° for 1 hr. before the viscosity was determined in the MacMichael apparatus. The hydrogen ion was determined, when possible, with the hydrogen electrode.

It has been observed that after definite time intervals the viscosity of caseins that have been subjected to pasteurizing temperature is always greater than that of caseins prepared at lower temperatures. If the solutions of caseins are allowed to stand a great length of time (24 hrs. or more) the viscosities tend to approach in value. In cases of caseins prepared under excessive temperatures, the difference in viscosity was so marked that careful control of reaction and time was unnecessary.

Table I—Viscosity and Physical Appearance of Some Commercial Caseins in Borax as Solvents, at 25° C.

Laboratory No.	Type	Ash Per cent	Viscosity Angular Degrees	pH of Soln.	Appearance of Solution
102-A	Cooked curd	4.27	430.0	...	Flakes
VI-C	Argentine	3.69	47.5	8.8	Flakes and milky
A-133(1)	Grain curd	0.64	61.0	9.0	Translucent
D-14	Commercial grain curd	2.55	50.9	9.0	Translucent
97-D	Natural sour	1.49	52.2	8.9	Smooth; slightly milky
104-B	Commercial sulfuric	5.12	276.0	...	Flakes
103-B	Cookedcurd	60.3	306.0	...	Flakes
M-10	"Nach Hammarsten"	1.07	69.8	9.0	Clear

In all cases, in the preparation of solutions of caseins in alkali solvents, temperatures above 30° C. were avoided; the viscosities were usually read at 25° C. It should be mentioned in this connection that the failure to apply successfully the viscosimeter to the analysis of commercial casein in the past may be attributed to the high temperatures and uncontrolled conditions employed. A glance at Table I will show that in general these caseins yielding high viscosities contained high ash, whereas not all high-ash caseins gave high viscosities. High-ash caseins which have been subjected to high temperatures always dissolve slowly at low solution temperatures, and, as a rule, are the caseins which are unpopular commercially.

From the viscosity curve (Fig. 1) of the best quality of casein ("nach Hammarsten") on borax, it is found that the viscosity of casein-borax solutions reaches a maximum at an H^+-ion concentration of about pH 8.15, or when 9.5 g. of anhydrous and ash-free casein are dissolved in 150 cc. of solution containing 40 cc. of 0.2 *M* sodium borate. The ascent of the curve is steep on approaching this point from the acid side. A complete solution is obtained with 9.5 g. of casein in 150 cc. of solution containing 10 cc. of 0.2 *M* borax, but the viscosity is much less. Upon the alkaline side of the maximum viscosity the drop is quite as precipitous, and at a pH of 8.9 to 9.1 the viscosity is practically constant, even though the quantity of solvent is increased in the order of 60 to 100 cc. of 0.2 *M* borax to 9.5 g. of casein. The concentration of casein was the same in each total volume of solution, the concentration of borax being the only variant.

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[1] Published by permission of the Secretary of Agriculture

[2] U. S. Department of Agriculture, *Bulletin* **661** (1918).

[3] *Paper*, **24** (1919), 217.

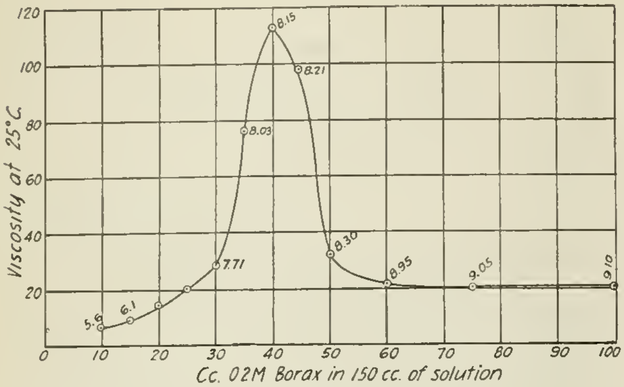

Fig. 1—Viscosity Curve of Casein-Borax Solutions. Concentration of Anhydrous Casein 6.5 Per cent. Hydrogen-Electrode Values Expressed in pH Are Given for Several Points on the Curve

In choosing the correct reaction for the casein-borax solubility test it is necessary to avoid the region of greatest viscosity changes, since contaminating substances in the commercial casein naturally influence the reaction of the mix, and when this occurs in the aforementioned region erroneous interpretations would follow. For example, we might have a casein from heated milk checking the viscosity of a normal casein possessing a medium content of acid salts as a result of the natural-sour process of manufacture. This has also been the experience in several instances in applying the commercial solubility test mentioned above. Naturally, the zone in which least viscosity change occurs is in that zone of maximum buffer action of the solution—beyond 9.0. The pH of a 0.2 *M* sodium biborate solution is approximately 9.13 (hydrogen electrode); the curve in Fig. 1 shows that in this region the viscosity is constant. This is the zone to which the reaction of the solutions in the improved method is adjusted.

The concentration of casein chosen for the improved casein-borax test is about 12 per cent of anhydrous 15 per cent casein[1] by weight. Chick and Martin[2] showed that the viscosity of casein in sodium hydroxide rapidly increased when the concentration approached 10 per cent. This was verified with "nach Hammarsten" by the writer, and also with grain curd (C. P.). The curve in Fig. 2 illustrates the point under discussion. The measurements were made with a MacMichael "universal" viscosimeter using torsion wire No. 000. Each solution was adjusted to the same reaction before measurement (pH 9.0), and temperatures above 30° C. were avoided in preparing the solutions. The viscosity became unmeasurable at concentrations of 14 per cent. Those caseins which tend toward gel formation exhibit it strongly at this concentration, while those that remain fluid at this concentration still flow rather freely.

A second important change from the ordinary procedure is to use much lower temperatures in the test. At temperatures around 40° C. and above, casein solutions change physically. In a succeeding paper the writer will present data to show that the hydrophylic nature of casein is sensitive to pasteurizing temperatures. Accordingly, a working temperature of 30° C. is advocated. This is chosen also for another reason. Complex borax solutions change internally at 35.5° C.[1] Above this temperature the pentahydrate may exist and deposit crystals from such a supersaturated solution; below this point the decahydrate separates. The latter is ordinary borax. A 0.2 *M* solution of borax is unsaturated at 30° C., but deposits crystals at 25° C. upon standing undisturbed.

REVISED METHODS

The casein is ground to pass a 40-mesh sieve; 15 g. of the casein are measured into a 250-cc. beaker; 100 cc. of 0.2 *M* borax at 30° C. (76.32 g. of $Na_2B_4O_7.10H_2O$ diluted to 1 liter) are added with vigorous stirring. This is allowed to stand for 30 min., with thorough stirring at intervals of 5 min. During the first 5 min. the mixture should be stirred rather frequently. A casein of known purity and conduct should be used as control until thorough familiarity with the method is gained. Usually the character of the casein shows up during the first 10 min., but 30 min. is advised for safety. Longer periods are unsatisfactory because of difficulty in interpretation.

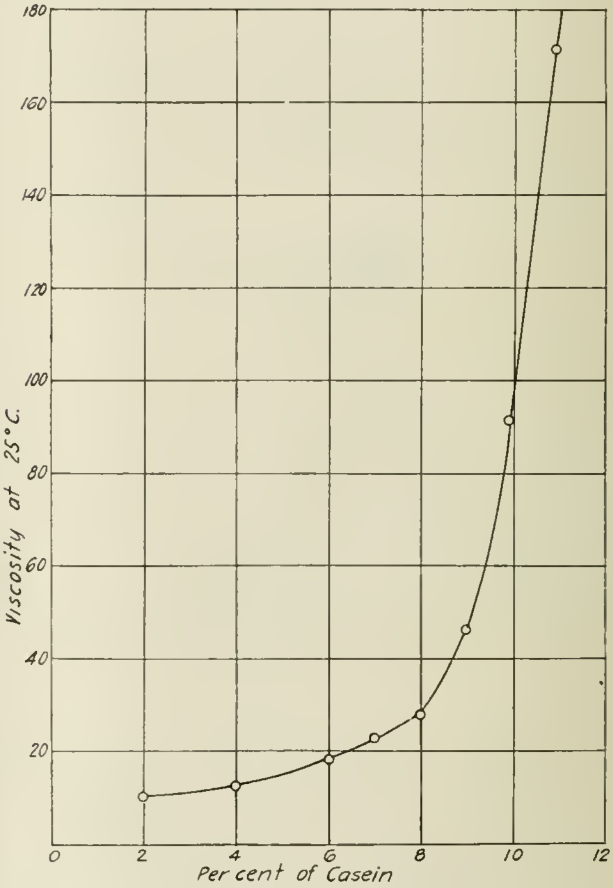

Fig. 2—Viscosity-Concentration Curve of Casein in NaOH. pH Maintained Constant at 9.0

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[1] The method calls for 15 g. casein in 100 cc. borate solution. The commercial caseins contain about 10 per cent moisture, 4 to 5 per cent ash, and some fat and sugar; perhaps 20 per cent of the commercial sample will consist of material not casein.

[2] *Kolloid-Z.*, **11** (1902), 102.

[1] Van't Hoff and Blasdale, *Sitzb. Akad. Wiss. Berlin*, **1086** (1905).

CAUTIONS TO BE OBSERVED IN THE PERFORMANCE OF THE TEST

1—Casein of low salt content is wetted with water slowly; hence when adding the 0.2 *M* borax solution to the casein it must be done with rapid stirring; otherwise lumps will form which dissolve at a slow rate. High fat content casein also wets slowly.

2—High solution temperature (above 35° C.) must be avoided, else the results become uninterpretable from the standpoint of the physical nature of both the casein and the solvent.

3—Casein which contains much fat behaves differently from others. It acts much like high temperature casein during the early stages of the test; *viz.*, it dissolves slowly and tends to form a gel simulating dilute gelatin or agar. If it is not a heated casein it begins to disperse after 15 or 20 min., with frequent stirring, and at the end of 30 min. it may be entirely dissolved, but the solution will be very milky and its consistence less cohesive or less mucilaginous than that of a casein without much fat. If it is a high-temperature casein containing much fat, the solution is irregular, milky, and gelatinous at the end of 30 min.

The following tabulation (Table II) shows the relative consistence and some physical appearances of caseins when treated as in the revised test.

TABLE II

Type of Casein and Method of Manufacture	Physical Consistence of Solutions in 0.2 *M* Borax	
	After 15 min.	After 30 min.
Commercial sulfuric; temperature 120° F.; ash 5.04 per cent	Stiff gel; undissolved; clear	Stiff gel; some undissolved; clear
Natural sour; low temp.; ash 3.69 per cent	Mostly dissolved; smooth; mucilaginous[1]	In solution; smooth; mucilaginous
Kahlbaum casein "nach Hammarsten;" low temp.	Dissolved; smooth and clear; mucilaginous	Dissolved; smooth and clear; mucilaginous
Cooked curd sulfuric; temp. 128° F.; ash 5.58 per cent	Stiff gel; undissolved; clear	Stiff gel; undissolved; clear
Modified cooked curd; temp. 120° F.; hydrochloric acid; ash 4.82 per cent	Gelatinous; much dissolved; cohesive	Still very gelatinous; some undissolved; cohesive
Grain curd; hydrochloric; temp. 95° F.; ash 2.55 per cent	Dissolved; clear; smooth solution; mucilaginous	Dissolved; clear and smooth; mucilaginous
Natural sour; high fat; fat 9.5 per cent; no history of temperature	Gelatinous; undissolved; milky white	Mostly dissolved; milky; cohesiveness poor
Buttermilk; natural sour; temp. 120° F.; fat 4 per cent	Stiff gel; undissolved; somewhat milky	Gelatinous; mostly dissolved; cohesiveness poor
Neutralized cream buttermilk casein; temp. 150° F. for 50 min.; precipitated at 125° F.; purified to an ash of 1.07 per cent	Gelatinized in chunks; undissolved; translucent	Mucilaginous; mostly dissolved; translucent.

[1] Mucilaginous is used in the sense of describing a very sticky fluid, and connotes cohesiveness.

The chief value of the borax test is to determine whether the casein under examination exhibits suitable working properties, when dissolved by certain alkalies. It should be borne in mind that it is not designed to give direct evidence of the actual value of a casein for glue making, paper sizing, paint preparation, or any other industrial product. Only direct and unprejudiced trial will determine the actual value. But the method as revised does serve to classify differentially the caseins according to certain inherent properties, depending upon the source and method of separation. It very rigidly differentiates between high- and low-temperature caseins. The cooked-curd caseins without fail tend to imbibe water and form a jelly in this test. They are also unsuitable for certain industrial operations, but are valuable for others. The test also serves to give evidence of the presence of fat in casein. It readily isolates those caseins which dissolve quickly to give solutions of even fluidity and translucence.

While the principle of this test is founded in viscosity phenomena, the use of a viscosimeter is avoided by choosing concentrations and conditions which yield viscosity data of interpretable value by a simple test.

It was a matter of great satisfaction to find that the casein produced by the grain-curd process without heat treatment, and with the idea of isolating casein by the most direct method, yields uniform and promising solutions with the improved borax solubility test.

SUMMARY

1—The viscosity curve of casein in borax solutions shows that the maximum viscosity is obtained at a H^+-ion concentration of pH 8.15, while at a pH of 8.9 to 9.1 the viscosity is less but constant, owing to the buffer effect of borax in this region. The importance of conducting the borax test in this buffeted region is discussed.

2—The great variation in the viscosity of casein solutions at different concentrations of casein is utilized in the improved test by choosing a concentration which will bring out the difference in physical constitution of casein prepared under safe and dangerous temperature conditions.

3—The viscosities of several caseins in borax solutions are given to show that differences in the physical structure of caseins have greater influence upon their viscosity than the normal contaminating substances present in commercial caseins. High-temperature caseins always exhibit a comparatively great initial viscosity.

4—The essential changes in the improved casein-borax test include low solution temperatures, reduced concentration of casein, and increased concentration of borax. These changes are based upon purely physicochemical relationships.

5—The value of the casein-borax test is defined as an accurate means of differentiating between low- and high-temperature caseins.

CELLULOSE ACETATES

By J. O. Zdanowich
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Received August 12, 1920

During the war, when cellulose acetate was found the most suitable material for aëroplane "dope," complaint was often made of the quantity and also the quality of the material at hand. With the active encouragement of the British Air Inventions Committee the writer has developed a new process[1] for the manufacture of cellulose acetates, which is even more successful on a large scale than in the laboratory, and which offers a considerable application in the manufacture of films, dopes, lacquers, and artificial silk.

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[1] U. S. Patent 1,347,801 (July 1920).

DESCRIPTION OF PRODUCT

The acetates prepared by this method are perfectly white, and dissolve very quickly, with almost no residue, and without passing through the gel state, showing that the conversion of cellulose into acetates is complete. Their acetone or acetone-alcohol solutions are remarkably clear.

The most characteristic feature, however, is the exceptionally low viscosity of the solutions. A 25 per cent solution, of the same viscosity as 8 to 10 per cent solutions of other acetates, is easily obtained. This property makes possible great economy of solvents in the commercial application of the acetates. For instance, to get a deposit of a given weight on an aëroplane wing, only two coatings, instead of four or five, are necessary.

It should also be added that by slightly varying the method of production, viscosity may be varied within certain limits.

In the manufacture of artificial silk and films, the new product is very valuable, inasmuch as the method of manufacture makes it possible to use the acetylating mixture directly for spinning threads, without previous precipitation

DESCRIPTION OF PROCESS

The characteristic feature of the process consists in the substitution of organic acids, especially chloroacetic acids, in the nascent state, for sulfuric acid by adding a halogen to the acetylating mixture. These acids have no injurious effect on the cellulose molecule at any temperature. After the mono- and diacetates are formed, the esterification becomes slow, but the addition of 1 per cent or less of sulfuric acid, or some other powerful condensing agent, readily completes the reaction. The product is a clear, colorless, viscous solution. It can be precipitated with water in the form of colorless, transparent films or threads. Moreover, such acetylating mixtures can be kept for many days without change, and can be used for spinning or for film production.

From the point of view of economy, there is no waste in large-scale production. The acetylating mixture or any of the waste may, if desired, be submitted to further hydrolysis, in order to obtain acetates entirely soluble in acetone or acetone-alcohol, which can be used for the manufacture of lacquers, varnishes, dopes, etc.

Government reports on the product are as follows:

Three samples have been examined at the A.I.D. laboratories, with the following results:

Sample	34	36	37
Moisture, per cent	4.80	5.05	5.12
Ash, per cent	0.10	0.05	0.06
Viscosity in acetone (6.100) at 25° C.	2.0	2.8	2.4
Viscosity in dope solvent (8.5 to 100) at 25° C.	7.4	9.3	10.0
Viscosity according to D. 6	39.0	42.0	44.0
Acidity (as HAc), per cent	0.014	0.018	0.014
Sulfate content as SO_4, per cent	0.22	0.35	0.27
Heat test—A, ° C.	198	199	198
Heat test—B, ° C.	209	209	203

The amount of moisture present in the three samples is quite normal, while the ash is quite low. No unusual constituents appeared to be present.

In spite of the large size of the fragments all the samples dissolved rapidly in both acetone and dope solvent, the process being apparently rather erosion than intermediate gel formation. The solutions thus obtained, apart from a few small fragments of undissolved material, were remarkably clear, the clarities of the acetone solutions reading 25, 20, and 25; the first and last are regarded as records in this respect.

The acidity shows a high tendency, though the amount is below the limit specified, while all the samples behaved satisfactorily under the heat test.

The characteristic feature of the solutions is their low viscosity, all being much below the optimum figure. On evaporation from dope solvents without plastics, all leave remarkably clear films. With plastics present, the films are in all cases flexible.

FRAME TESTS—Dopes made up with the above samples of cellulose acetate according to Formula D100.4A (*a*) were examined with the following results:

	34	36	37
Viscosity	7.4	9.3	10.0
Film	12.5	12.5	12.5
Character of film	Clear, tough, and flexible		

Frame tests showed that by brushing three coats on to standard linen fabric fair tautness was obtained with added weights per square yard of

34—1.1 oz.
36—1.0 oz.
37—1.0 oz.

It is possible that by making a more concentrated second coat, only two coats need be applied. There was, however, insufficient material submitted to try this.

A weathering test on a sample of dope made from Sample 37 has been running since August 1918 till the end of December. The surface of the dope film remained intact, and there were no signs of deterioration.

So far as weathering is concerned the result may be considered quite satisfactory.

SUMMARY

The advantages of this process over the viscose process for the manufacture of artificial silk are as follows:

1—The process is shorter and less complicated.

2—The acetylating mixture, which can be prepared in half the time required for the viscose solution, remains unaltered for days, and can be used for spinning during that time.

3—The precipitation is effected in water, and the yarns so produced are practically ready for use without further treatment.

4—Through the entire process, none of the material handled is injurious to the health, as compared with the viscose process where carbon bisulfide is used.

THE DIRECT IDENTIFICATION OF SOY-BEAN OIL

By Charles A. Newhall
6303—21st Ave., N. E., Seattle, Washington

Received June 2, 1920

Oil chemists seem to have overlooked a valuable test for the direct identification of soy-bean oil. Two color tests attributed to L. Settini[1] have been found of value in detecting admixtures of soy-bean oil with other commercial oils.

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[1] *Chem. Abs.*, **7** (1913), 908.

For some three years the writer has been using a modification of the second test, as follows:

Five cc. of chloroform are added to 5 cc. of the oil, mixed in a small test tube with a few drops of gum arabic solution and 5 cc. of a two per cent solution of uranium nitrate or uranium acetate, and shaken to form a thorough emulsion. All samples of crude and refined soy-bean oil so far examined give a characteristic lemon-yellow emulsion, whereas no other oil so far tested gives this color.

The most valuable use for the test has been in detecting admixtures of the cheap bean oil with high-priced wood oil or with linseed oil. With the former the test is sharp, it being possible to detect as low as 5 per cent of bean oil. The test is conducted by comparison with blends made up with pure wood oil and pure bean oil.

With linseed oil the test is not so sharp, as linseed oil mixtures always give a slightly brownish color. It has never been absolutely certain that the linseed oil samples used for comparison were pure, and further work is in progress.

With such oils as peanut, cottonseed, sesame, rape, and coconut, the test is very sharp, as these oils give white or slightly colored emulsions with the uranium salt.

The yellow emulsion is not formed with bleached and deodorized bean oil, hydrogenated oil, or bean oil fatty acid.

This Settini test for bean oil is not as sharp as some of the direct color tests characteristic of sesame or cottonseed oils, but nevertheless it has been of great value in the commercial testing of oils arriving from the Orient. This is no indication that it will work equally well with domestic soy-bean oil. Since the yellow emulsion seems to be due to the presence of coloring matter in the crude oil rather than to some substance inherent to the oil, this coloring matter may be characteristic of only certain varieties of soy bean. Until the exact nature of the yellow emulsion is cleared up, the Settini test should be used with caution, and its limitations taken into account.

THE OIL OF THE PRICKLY PEAR SEED[1]

By S. Lomanitz

College Station, Texas

The prickly pear is offered for sale as a refreshing fruit at street corners in Mexican towns. In some places the pulp is made into a delicious hardened jelly and put up in form of bricks. These jelly bricks, *panes* or *quesos* (literally cheeses), as they are called, possess very good keeping qualities and can be found for sale in candy and confectionery stores all through Mexico, a goodly number of them finding their way even into this country. In making these quesos the seeds are disposed of as waste.

Analysis of the seeds of a more or less cultivated variety of white prickly pear, known as *tuna blaca de huerta*, gave the following result:

	Per cent
Moisture	7.68
Ash	2.96
Oil	10.89

The oil, which was obtained by extracting the seed with petroleum ether, was greenish yellow in color, odorless, and somewhat viscous at ordinary temperatures.

The following constants of the oil were determined according to the methods recommended by Lewkowitsch.

Specific gravity, 15.5/15.5	0.9294
Acid number	3.09
Free fatty acids, as oleic acid	1.55
Saponification value	189.5
Iodine number	116.30
Ester number	186.47
Reichert-Meissl number	2.8
Habner number	93.81
Index of refraction, n_D^{40}	1.46764

From the data on hand, the oil apparently falls into the group of semi-drying oils, and produced in sufficient quantities might be used in some of the oil-products industries.

THE DETERMINATION OF CRUDE FIBER IN PREPARED MUSTARD

By M. C. Albrech

The R. T. French Co., Rochester, N. Y.

Received May 27, 1920

The method for the determination of crude fiber in prepared mustard given in the *Journal of the Association of Official Agricultural Chemists*[1] differs from the general method for crude fiber in that the fat is not extracted before treating with 1.25 per cent sulfuric acid, it evidently being considered impracticable to do so.

Upon investigation of the present method by the author it was discovered that while certain samples gave results which might be somewhere near the true figure for crude fiber, other samples gave results clearly impossible. Samples of prepared mustard which contained little oil gave better results than samples which contained a larger amount, showing clearly that the oil interferes with the method, and gives results much too high. Washing with alcohol and ether to remove residual oil after treatment with acid and alkali, would, of course, not prevent the interfering action of the oil during the operation.

The method devised to correct this defect consists in a preliminary treatment of the prepared mustard, as follows: 8 g. of the material are weighed into a 500-cc. Erlenmeyer flask, 100 cc. of boiling water are added, and the flask stoppered and shaken vigorously, to disintegrate the prepared mustard. The solution is then immediately filtered on a filter paper on a Büchner funnel, and the residue is immediately washed with alcohol, then with ether repeatedly, until the fat is removed and the ether washings are colorless. The material remaining on the paper is immediately washed, or carefully scraped and washed off the filter with 200 cc. of boiling, 1.25 per cent, sulfuric acid, and the determination completed according to the regular method, the final fiber being weighed on a tared filter paper with suitable precautions. Under the proper conditions the preliminary treatment can be carried through without much difficulty. It is essential to carry the preliminary treatment through without pause between the operations, as otherwise the fiber will dry on the filter and much difficulty will be encountered.

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[1] Read before the Central Texas Section of the American Chemical Society, May 7, 1920.

[1] **2**, No. 3, Part 2

The results obtained by the two methods on several samples of prepared mustard are as follows:

				Official Method		New Method	
No.	Solids	Ether Extract	Salt	Crude Fiber	Crude Fiber on Dry, Salt- and Fat-Free Basis	Crude Fiber	Crude Fiber on Dry, Salt- and Fat-Free Basis
1...	18.36	4.54	4.14	1.90	19.63	1.00	10.33
2...	18.70	4.63	4.14	2.21	21.66	1.00	9.80
3...	16.97	4.99	2.74	2.16	22.88	0.92	9.74
	.....	....	....	1.77	18.75	0.77	8.15

It will be noted that in some cases the error in the official method is over 100 per cent.

Another point to be considered in the determination of crude fiber is that duplicates are often considered satisfactory if they do not differ more than 0.2 per cent. This value, when calculated on a dry, fat- and salt-free basis, will mean a difference of as much as 2 per cent crude fiber in certain samples of prepared mustard.

SUMMARY

1—It has been shown that the official method for the determination of crude fiber in prepared mustard is fundamentally defective, giving high results because the oil is not extracted before treatment with acid, as in the usual method.

2—A preliminary treatment has been devised which eliminates the defect in question.

3—It is pointed out that in judging prepared mustards consideration must be given to the large error which may arise when results are calculated to the dry, fat- and salt-free basis.

ORANGE VINEGAR—ITS MANUFACTURE AND COMPOSITION

By Homer D. Poore

Citrus By-Products Laboratory, Bureau of Chemistry, U. S. Department of Agriculture, Los Angeles, Cal.

Received July 20, 1920

Oranges, because of the high sugar content of their juice as compared with most other citrus fruits, will produce a vinegar of as good quality as the best grades of apple cider vinegar. The large amount of cull fruit available in California and Florida offers a source for the production of orange vinegar on a commercial scale. In the years when freezes occur, much more than the average amount of fruit is unmarketable, and although the yield of juice from frozen fruit is considerably less than from sound, the actual cost of the fruit to the purchaser is much smaller and the quality of the vinegar is not impaired.

DESCRIPTION OF PROCESSES OF MANUFACTURE

Two processes have been tried out at this laboratory; one to make vinegar on a small scale for home use by the barrel or roller process, and the other to produce it on a commercial scale by the well-known rapid or generator process. The barrel process produces only 30 to 40 gal. per unit and requires from 60 to 90 days, while the generator process yields from 20 to 150 gal. per 24 hrs., according to the size of the generator.

BARREL PROCESS—The experimental work on the barrel process was carried out by C. P. Wilson, and the analyses of vinegars obtained by him are given in Table I. Briefly, the process consists of carrying out the alcoholic fermentation of the juice with yeast, and then placing it in a generator made by dividing a barrel into two compartments by means of a rack running lengthwise. One compartment occupying about one-fifth of the space is filled with beechwood shavings or corncobs saturated with unpasteurized vinegar. Three one-inch holes bored in each end just below the rack allow air to pass through the shavings. The fermented juice is placed in the larger compartment and the barrel rolled two or three times a day, with the holes plugged, in order to bring the cider in contact with the acetic ferment on the shavings.

GENERATOR PROCESS—This paper will take up the rapid process, as carried out on a scale that produces vinegar practically as it would be obtained in a manufacturing plant. The generator was one of the smaller standard sizes, those generally used having a capacity from five to fifteen times as great. It consisted of a cylindrical tank 6 ft. high and 3 ft. in diameter, with a perforated false bottom 1 ft. from the bottom, on which rested beechwood shavings for a height of 4 ft. Above the shavings was a perforated distributing head on which was set an automatic dumping trough. Between the true and false bottoms, six holes were bored obliquely through the staves of the generator, through which the entrance of air was regulated by means of plugs. A long-stemmed thermometer was inserted in a hole bored at about the center of the side.

EXPERIMENTAL WORK

Five runs of vinegar were made, two from sound fruit and three from frozen. The juice was expressed with a hydraulic press and the alcoholic fermentation carried out in from 2 to 5 days by inoculating with bakers' yeast and maintaining a temperature of about 86° F. The juice was then filtered through a DeLaval clarifier and filter, and started through the generator. For the first run, the shavings were seeded with the vinegar bacteria by adding 5 gal. of unpasteurized apple vinegar after the generator had been sterilized with steam. Fifty gallons of juice were used, and as the shavings were saturated with water and cider vinegar at the start, the resultant vinegar contained only 4.32 g. of total acid as acetic. This first lot was, therefore, not wholly orange vinegar, and was used only to acidulate the shavings for the second lot.

In the second run, 2500 lbs. of sound culls yielded 80 gal. of juice, or 64 gal. per ton. The generator was sterilized with live steam, 10 gal. of Lot 1 added to the shavings, and the fermented juice or cider run through. Both of these vinegars were produced in August when the room temperature varied from 70° F. at night to 90° F. during the day. No one was on duty at night to regulate the amount of air and flow of juice, and although little difficulty was experienced in maintaining the best temperature for oxidation, 86° F., during the day, it was impossible to regulate the flow and air openings when leaving at night so as to maintain the required temperature. In the morning the thermometer registered between 99° and 112° F., and generally all of the juice had run through. Because of the small size of the generator it was necessary to pass the juice through several times, and a total of seven days was required for each of Lots 1 and 2.

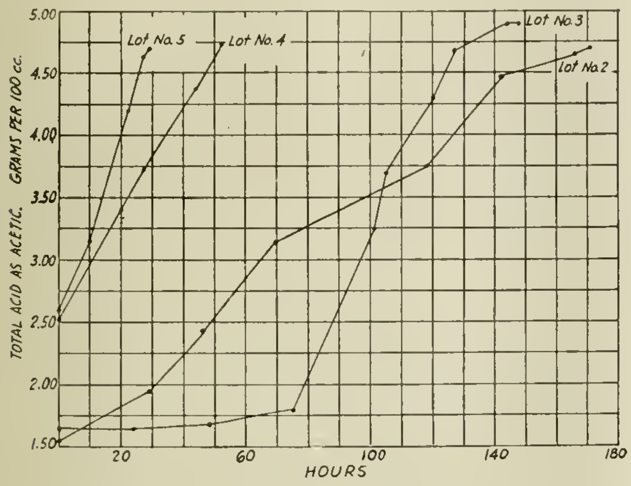

Fig. 1—Rate of Generation of Acetic Acid

From the experience gained in making these two lots, much better results were obtained with the three succeeding lots. The day of 24 hrs. was divided into three shifts, and one man was on duty continually, so that the generator received constant attention.

For these three lots, 39, 42, and 35 gal. of juice were expressed from 1750, 1950, and 1600 lbs., respectively, of badly frozen navel oranges, an average of 44 gal. per ton of fruit. The work was carried out in March when the room temperature varied between 45° and 65° F. The generator was steamed, clean, dry, shavings placed in the middle compartment, 9 gal. of vinegar of Lot 1 added, and the 39 gal. of cider of Lot 3 run through. The generator and room proved to be too cold for oxidation to start; so about 10 gal., warmed to 100° F., were run in. Action began in a short time, as shown by titration. The time required to produce the vinegar after action started was 74 hrs. The dry shavings absorbed 26 gal. of liquid, which was left in them when the fourth lot of 42 gal. of cider was started. Likewise 26 gal. of Lot 4 remained to acidulate the shavings for the fifth lot. The time required for Lots 4 and 5 was 52 and 29 hrs., respectively, the working of the generator being as nearly perfect as possible in the last run. The rate of generation of acetic acid in the different runs is shown graphically in Fig. 1.

In many cider vinegar plants it is the practice to allow the juice to ferment spontaneously in large vats of as high as 26,000 gal. capacity. This may take several months, during which time practically all sediment has settled out so that it is unnecessary to filter before passing into the generators. It is also customary to mix one part of vinegar with two parts of cider, and run this mixture into the generators, which vary from 4 by 12 ft. to 6 by 16 ft. The resultant mixture of the cider of Lots 4 and 5 with the 26 gal. of vinegar left in the generator from the previous run was about the same as a 2 : 1 mixture.

COMPOSITION

Table I shows the analyses of three lots of vinegar made by the barrel process. The alcoholic content of Lot 3 is greater than the law allows, but a few months' aging would cause it to decrease to below 0.5 per cent.

Table I—Analysis of Vinegars Made by Barrel Process (Results in Grams per 100 Cc.)

Lot Number	1	2	3
Total acid as acetic	5.97	5.52	6.03
Volatile acid as acetic	5.09	4.52	5.06
Fixed acid as citric	1.03	1.16	1.13
Alcohol (per cent by volume)	0.50	0.39	0.75
Total solids	2.99	..	2.96
Ash	0.48	..	0.47
Water-insoluble ash	0.08	..	0.11
Alkalinity of water-soluble ash (cc. 0.1 *N* HCl per 100 cc.)	45.1	..	40.8

Table II shows the composition of vinegars made by the generator process, analyzed according to the methods of the Association of Official Agricultural Chemists.

Table III shows the analyses of the fresh juice, cider mixture, and vinegar of Lots 4 and 5 at the different stages of the generator process. It will be noted that the final vinegar contains nearly all of the fixed acid calculated as citric that was present in the juice. The heavy lead precipitate is due to the citric acid.

The solids, ash, P_2O_6, and alcohol precipitate are

Table II—Analyses of Vinegars Made by the Generator Process (Results in Grams per 100 Cc.)

Lot Number	2		3	4		5		A[1]
Elapsed time in months between date of preparation and date of analysis	2	9	0	0	4	0	4	
Specific gravity $^{15.6}/_{15.6}$	1.0209	1.0224	1.0277	1.0229	1.0240	1.0217	1.0225	...
Alcohol per cent by (volume)	0.36	0.07	0.03	0.43	0.34	0.37	0.26	...
Glycerol	0.25	0.22	0.24	0.22	0.23	0.21	0.21	...
Solids	3.82	4.03	5.26	4.34	4.50	4.02	4.12	2.49
Non-sugar solids	...	3.81	...	...	4.21	...	3.88	...
Total reducing substances before inversion	0.16	0.25	0.19	0.20	0.33	0.17	0.25	0.25
Reducing sugars before inversion after evaporation	...	0.22	...	...	0.29	...	0.24	...
Reducing sugars after inversion	...	0.22	...	...	0.29	...	0.24	0.25
Total ash	0.52	0.54	0.79	0.61	0.64	0.55	0.57	0.34
Water-insoluble ash	0.15	0.16	0.29	0.17	0.17	0.14	0.15	...
Water-soluble ash	0.37	0.38	0.50	0.44	0.47	0.41	0.42	...
Alkalinity of water-soluble ash (cc. 0.1 *N* HCl per 100 cc.)	44.0	48.0	64.0	55.2	57.2	53.2	54.0	...
Total P_2O_6 (mg. per 100 cc.)	44.9	45.6	53.0	38.8	41.9	35.1	36.3	34.8
Total acid as acetic	4.72	5.02	4.91	4.74	4.98	4.70	4.91	...
Fixed acid as citric	1.00	1.00	1.20	1.07	1.07	1.04	1.04	0.11 (malic)
Volatile acid as acetic	3.79	4.08	3.79	3.74	3.98	3.73	3.93	4.84
Protein (N × 6.25)	...	0.75	...	...	0.61	...	0.56	...
Lead precipitate	Very heavy	Very heavy	Very heavy	Very heavy	Very heavy	Very heavy	Very heavy	...
Alcohol precipitate	...	1.06	...	...	1.12	...	0.95	...

[1] These results, which are inserted for comparison, are taken from page 761 of "Food Inspection and Analysis" by Leach, and give the average analyses of twenty-two samples of cider vinegar of known purity made by H. C. Lythgoe.

Table III—Changes in Composition Occurring during the Generator Process

Lot Number	4				5			
	Fresh Juice	Fermented Juice	A[1]	Vinegar	Fresh Juice	Fermented Juice	A[1]	Vinegar
Total acid as citric	1.14	1.13	...	...	1.14	1.14	...	...
Total acid as acetic	...	...	2.53	4.74	...	...	2.63	4.70
Fixed acid as citric	1.12	1.03	1.09	1.07	1.13	1.07	1.07	1.04
Volatile acid as acetic	...	0.09	1.50	3.74	...	0.07	1.63	3.73
Total solids	13.39	3.64	4.26	4.34	13.49	3.43	3.81	4.02
Total sugars as invert	9.91	...	...	0.20	9.87	...	...	0.17
Alcohol per cent by (volume)	...	5.73	3.55	0.43	...	5.75	3.48	0.37
Total ash	...	0.48	0.60	0.61	...	0.46	0.52	0.55
Water-insoluble ash	...	0.10	0.17	0.17	...	0.09	0.12	0.14
Water-soluble ash	...	0.38	0.43	0.44	...	0.37	0.40	0.41
Alkalinity of water-soluble ash (cc. 0.1 *N* HCl per 100 cc.)	...	51.2	56.1	55.2	...	50.0	52.1	53.2

[1] The calculated analyses of the mixture consisting of the vinegar left in the generator from the previous run and the fermented juice of this run.

Table IV—Production Cost per Gallon of Orange Vinegar

Cost per Ton of Fruit	Cost per Gallon Raw Juice	Total Manufacturing Cost and Overhead	Bottles and Caps (C. L.)	Labels	Breakage, Waste, etc.	Cooperage	Loss	Total
				Best Labels and $^{1}/_{5}$-Gallon Bottles				
$3.00	$0.043	$0.10	$0.264	$0.01	$0.009	..	..	$0.426
5.00	0.071	0.10	0.264	0.01	0.01	..	..	0.457
10.00	0.143	0.10	0.264	0.01	0.011	..	..	0.528
15.00	0.214	0.10	0.264	0.01	0.013	..	..	0.601
20.00	0.286	0.10	0.264	0.01	0.014	..	..	0.674
				Cheaper Labels and Full Quart Bottles				
3.00	0.043	0.10	0.271	0.006	0.009	..	..	0.429
5.00	0.071	0.10	0.271	0.006	0.010	..	..	0.458
10.00	0.143	0.10	0.271	0.006	0.011	..	..	0.531
15.00	0.214	0.10	0.271	0.006	0.013	..	..	0.604
20.00	0.286	0.10	0.271	0.006	0.014	..	..	0.677
				In Old Whisky or Brandy Barrels				
3.00	0.043	0.10	..	..	..	$0.11	$0.003	0.256
5.00	0.071	0.10	..	..	..	0.11	0.003	0.284
10.00	0.143	0.10	..	..	..	0.11	0.004	0.357
15.00	0.214	0.10	..	..	..	0.11	0.005	0.429
20.00	0.286	0.10	..	..	..	0.11	0.005	0.501
				In Old Vinegar Barrels				
3.00	0.043	0.10	..	..	..	0.06	0.003	0.206
5.00	0.071	0.10	..	..	..	0.06	0.003	0.234
10.00	0.143	0.10	..	..	..	0.06	0.004	0.307
15.00	0.214	0.10	..	..	..	0.06	0.004	0.378
20.00	0.286	0.10	..	..	..	0.06	0.005	0.451

higher than the averages of cider vinegar. The fixed acid is very much higher, as cider vinegars contain only about 0.10 per cent.

Apple juice contains from 10 to 16 per cent of sugar, averaging about 12 per cent, while orange juice runs from 8 to 11 per cent with an average of 9.5 per cent. This 2.5 per cent difference in sugar means that orange vinegar will contain at least 1.15 per cent less acetic acid. However, the larger amount of fixed acid in orange vinegar brings the total acidity to about the same percentage as that of apple vinegar. The glycerol content of about 0.2 per cent corresponds to the amount of sugar present in the juice, cider vinegars made from juices with a higher percentage of sugar containing more glycerol.

The orange vinegars made by the barrel process are higher in acidity and more nearly the theoretical yield, because there is less evaporation of alcohol due to the lower temperature during generation. The increases in the various constituents except alcohol, noted after standing several months, are due no doubt to a slight evaporation through the barrels in which they were stored. The alcohol decreases, part of it changing to acetic acid, and part probably to esters, the latter adding to the aroma of the vinegar. It is considered best to leave about 0.3 or 0.4 per cent of alcohol, not only to improve the keeping qualities, but to insure a gradual formation of esters, just as in wine during aging.

Samples of orange vinegar that have been submitted to jobbers who make a business of handling vinegar have been pronounced as fine as the best grades of their product. The color, odor, and taste are practically the same as those of apple vinegar, no distinguishing characteristic being noted.

COST OF MANUFACTURE

With prices changing as they have been, it is impossible to estimate accurately the costs of equipment, material, and production. However, the price of apparatus was obtained in January 1920, and approximate costs of production at that time can be estimated from figures as received from apple vinegar manufacturers. Summaries only will be given here, but the costs of manufacturing in detail will be found in an article by E. M. Chace and the writer in recent issues of the *California Citrograph*[1] and *Florida Grower*.[2]

EQUIPMENT—The equipment for a small plant using a hand power hydraulic press, with a capacity of 250 gal. per day, would cost about $2000. A 2500 gal. or 50 bbl. plant would reach $3500, using a steam power hydraulic press. A continuous type press would add about 50 per cent to this estimate. For a 100 bbl. plant, the figures given can be doubled. These prices include pasteurizing, bottling, and filtering machines, which cost $800 and would be unnecessary if the product is barreled.

MATERIAL—Frozen fruit can be obtained for the cost of hauling, about $3 per ton, while sound fruit will run from this amount to $20 per ton. Frosted oranges will yield as low as 40 gal. per ton, while sound fruit will average about 70 gal.

PRODUCTION COSTS—Apples yield as high as 180 gal. of juice per ton, so that the figures obtained from vinegar manufacturers, which also included the cost of apples, are not comparable for oranges. However, all things considered, 10 cents a gallon should cover the cost of production, including overhead.

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[1] **5** (July 1920), 282.

[2] **22** (July 24, 1920), 4.

Table IV shows the cost of production per gallon under various conditions, based on a yield of 70 gal. per ton. Where frozen oranges are used with a 40 to 50 gal. yield, the cost per gallon of raw juice would be about seven cents.

Apple vinegar in bulk retails as low as 35 cents per gallon, so that with oranges at over $5 per ton, there is little chance to compete with cider vinegar. But put up in quart bottles under well-established brands, there is no reason why the product cannot compete with the fancy grades of cider vinegars, which retail in quart bottles from 80 cents to $1.40 per gallon.

It is necessary, because of the alcoholic fermentation, to obtain a permit from the Bureau of Internal Revenue in order to manufacture vinegar.

SUMMARY

Brief descriptions are given of the two processes used to produce orange vinegar, one in a small way by the roller process, and the other on a commercial scale, by the well-known generator process. This paper takes up the experimental work carried out on the latter process with five different lots of oranges, two of them sound fruit and three frozen.

Tables of analyses showing the changes that take place during the process and the composition of the vinegar obtained are given. Analyses of the vinegar after several months aging are also included, and comparisons made with apple vinegar.

The cost of manufacturing orange vinegar, including equipment, material, and production costs, is estimated from figures obtained from apple vinegar manufacturers.

ACKNOWLEDGMENT

The writer wishes to express his appreciation of the valuable assistance of Mr. E. M. Chace, under whose supervision the work was carried out.

RECENT ADVANCES IN DEFECATION[1]

By W. D. Horne

National Sugar Refining Company of New Jersey, Yonkers, N. Y.

Among the most recent improvements in defecating sugar solutions, two new clarifiers have been developed which give promise of good continuous separation of insoluble matters from sugar solutions, both in raw sugar making and in refining. The greater economy of time, labor, and fuel, as well as the smaller loss of sucrose, make these methods worthy of attention.

The Dorr thickener, long and favorably known in metallurgical work, has been developed under the name of the Dorr clarifier, so as to treat cane juice; and the initial run this spring at Central Mercedita, of the Cuban-American Sugar Company in the Province of Pinar del Rio, Cuba, was of great interest. A single unit, consisting mainly of a cylindrical apparatus 18 ft. in diameter by 10 ft. high, and containing two trays or transverse diaphragms, equipped with slowly revolving scraper mechanisms, handled practically all the juice from the 1500 tons of cane ground daily.

The cold juice was limed as usual, heated in the Deming heater to near the boiling point, and fed to the central loading-well of the clarifier. The sedimentation was very satisfactory and the clarified liquor flowing out of the peripheral pipes was much cleaner than that previously obtained from open defecators.

There was practically no inversion, and the juice thus treated was so clear it produced decidedly cleaner raw sugar than before. The mud was twice as concentrated as that ordinarily settled, carrying only about 5 per cent of the total juice. After diluting, it passed directly to the filter presses, with little or no further liming or heating.

The asbestos lagging on the tank retarded loss of heat so efficiently that the liquor entering at 207° F. left at 202° F., and the economy in coal, over what had been burned previously to maintain the temperature of juice in open defecators, amounted to about 8 tons per day.

Comparative records in defecating by the ordinary method from January 1 to March 20 and by the Dorr clarifier from March 20 to May 15 showed that although there was much more burnt cane during the second period, the milligrams of insoluble matter per 100 g. raw sugar dropped from 87 to 63, on the average, and 37 at the lowest. Cleanliness of raw sugars, on an arbitrary scale having 10 for the best, rose from 5.5 to 7.5 average, and 9 at best; sucrose in press cake fell from 6.75 to 5.5 per cent average, and 3.4 lowest; consumption of coal daily fell from 16.2 tons to 8.8 tons.

The Williamson clarifier is designed to separate all suspended and precipitated bodies from a sugar solution by flotation, with the aid of multitudes of minute air bubbles, which attach themselves to the insoluble matters and carry these impurities to the surface in the form of a very persistent scum. Thus far, the principal demonstrations have been afforded in the treatment of refinery washed sugar solutions at full working density of 60° Brix or over.

The sugar solution is defecated in some suitable manner, as with phosphatic preparations and milk of lime, and at a temperature of 135° to 140° forced through an aërating vertical pipe with an air blast at 20 lbs. pressure, all entering at the bottom and emerging above in an emulsified condition. This aërated liquor passes through a controlled feed pipe into the settling tank, 6 × 12 ft. and 2 ft. deep, with about 20 transverse steam heating pipes near the bottom and 6 vertical baffle plates evenly spaced and extending entirely across the tank, from the steam pipes to within a few inches of the liquor level. The temperature of the liquor rises gradually to 205°, causing the air bubbles to expand and rise to the surface, carrying the defecant and the fine, suspended, insoluble matters along with them. The baffles insure the even and slow passage of the liquor toward the outlet end, and the scum, unimpeded by the submerged baffles, passes along with it and is gently brushed over an inclined lip at the end of the tank by a 3-in. roller, extending across the full width of the tank, into the scum trough. The clear liquor is syphoned off continuously at the outlet end from a few inches below the surface, flowing through a regulating orifice made to deliver the requisite number of gallons per hour, while the feed device maintains a constant level.

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[1] Presented before the Section of Sugar Chemistry at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

In one of the trial runs 6375 gal. of washed sugar liquor at 63° Brix were treated in 6.75 hrs., or at the rate of 945 gal. per hour, with the production of 352 gal. of scum (3.65 per cent of the original solids). The clarified liquor passed to the char filters and the scum was twice washed by decantation, leaving 298 gal. to be filter-pressed, containing 1.05 per cent of the original solids. The pressed cake occupied a volume equal to 31 gal., and weighed 157 lbs. The purity of the press water was 93.3 as compared with 94.3 for the first dilution. There were produced 18.2 gal. of sweet water for 100 gal. of original liquor, and a considerable portion of that could be utilized in preparing succeeding washed sugar liquor. The invert sugar rose from 0.69 to 0.83 per cent in the liquor during treatment.

In another run 5,770,356 lbs. of washed sugar were treated in a week, defecating with 510 lbs. P_2O_5 per million pounds of washed sugar, with lime to neutralize. The rate of flow was 844 gal. per hour for each clarifier. 92.4 per cent of the dissolved solids passed into the liquor and 7.6 per cent into the scums, which weighed 9.11 lbs. per gal. and upon evaporation contained 61.14 per cent solids.

Of the scum, 53.77 per cent was filter-pressed; 46.23 per cent was first diluted, heated, settled, and the muddy portion then filtered, producing sweet water of 28.83 Brix. It is shown by calculation that if all the scum were defecated 97.35 per cent of the total solids entering the work would be recovered, of which 92.40 per cent would be in defecated liquor, 4.95 per cent in defecated sweet water, and 2.65 per cent in press sweet water from residual scums.

There was no inversion in the liquor. In the sweet water the glucose rose from 1.26 to 1.57 per cent (dry basis), and ash from 0.45 in liquor to 0.66 in sweet water from scum, and 0.82 in sweet water from filter pressing the residual mud.

The advantages of this mode of clarification are the doing away with bag filters and filter presses for the bulk of the liquor, and the consequent economy of labor in this arduous and mussy work. The introduction of automatic control apparatus also simplifies the labor and promises to give more uniform work and products.

THE CHEMISTRY OF DIGITALIS[1]

By Herbert C. Hamilton

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Few, if any, plants used in medicine have been the subject of such exhaustive research to discover the active principles and separate them in pure form as has digitalis. The list of investigators is seemingly endless; and the products resulting from their researches are equally numerous. While much of the recent work has been carried out primarily to obtain purified preparations adapted to certain particular purposes or modes of administration, with no specific attempt to isolate a single pure principle or to separate one from another if more than one are present, unquestionably the underlying thought is to accomplish this end.

This is shown by the products, such as digitalone, digipuratum, digipoten, and others, in which the resulting product is more or less purified and is probably better adapted to prompt therapeutic response than the average pharmaceutical.

The author has now succeeded in isolating from digitalis two active agents, although probably not in absolutely pure form. One of these is soluble in chloroform and the other insoluble, but solubility in this reagent is so dependent on the presence or absence of other constituents of digitalis or on a mixture of the two active agents that it is exceedingly difficult to arrive at a point where the complete solubility of the one or insolubility of the other can be established.

If an attempt is made to extract digitalis leaves with chloroform, no considerable amount of active matter is obtained in the extract. If one attempts even to use this as a solvent for Extract Digitalis, U. S. P., little of the active substance is dissolved. On the other hand, a mixture of alcohol and chloroform can be applied with greater success, and under certain conditions the whole of the active ingredients will be found in this mixture of solvents.

Again after a partial purification of a digitalis extract, by which the water-soluble inert substances have been removed, chloroform will dissolve all the active material along with the chlorophyll, both of the distinctly different constituents dissolving with equal facility.

It appears, therefore, that certain constituents prevent solution of either active agent in chloroform, while others aid solution, even permitting the ordinarily insoluble principle to dissolve.

By careful manipulation, however, removing first one and then another of the inactive constituents of the leaf, it is possible to arrive at a point where the product is sufficiently free from substances which affect its physical properties to permit the separation from each other of one substance soluble, the other insoluble in chloroform. Both are soluble in ethyl alcohol, neither entirely soluble in acetone, but this does not seem to indicate the presence of a mixture, the behavior toward acetone being so far unexplainable. Neither is more than slightly soluble in water alone, but the alcoholic solution of the chloroform-insoluble part is clearly soluble in water, even when only a minute amount of alcohol is present, while the chloroform-soluble part from an alcoholic solution gives a hazy solution when mixed with water.

The proportion of the two present in the leaf has not been determined with certainty, since variations are probably chargeable largely to non-quantitative separation. The average ratio, however, is approximately 2 parts chloroform-soluble to 3 parts chloroform-insoluble.

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[1] Presented before the Division of Biological Chemistry at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

The similarity of the pharmacologic effects of the two substances tends toward skepticism as to the correctness of this separation into two parts of dissimilar solubilities. The existence of the chloroform-insoluble part is unquestionable; but there seems to be a tendency for the soluble part to become less soluble on repeated applications of the solvent, or else conditions tend to favor the separation of more of the insoluble from the soluble. While such tendency toward increasing insolubility is a fact, the writer has never yet succeeded in obtaining an *inactive* chloroform-soluble portion. In all the work, pharmacologic experiments have demonstrated the presence or absence of an active agent at every stage of the process.

The activities of these two agents, in terms of the leaf of average potency considered as 1, are chloroform-insoluble 100, chloroform-soluble 70. It is evident, therefore, that the chloroform-insoluble principle is responsible for between 65 and 75 per cent of the potency of the leaf, as measured by the M.L.D. or M.S.D. on frogs.

Statements to the effect that the chloroform-soluble part is better adapted to therapeutic purposes than is the insoluble portion must be regarded with suspicion, first, because there appears to be no essential difference in the action of the two, and, second, because the complete separation of the two can be accomplished, if at all, only when in a high state of purity and where no trace of admixture of alcohol appears with the chloroform. At a certain stage in the process, by use of chloroform on a hydro-alcoholic solution of digitalis, one can obtain a separation, one part containing a large percentage of the active agents, the other containing only a small part, but this is merely an incomplete separation of the active from the inactive portion of the extract, mixed miscible solvents and not immiscible solvents being responsible for the completeness of the separation.

The object of presenting this subject in so unfinished a state is primarily to record what seems to be a material bit of progress in the chemistry of digitalis, and at the same time to question publicly any statement to the effect that it is a simple matter to separate the chloroform-soluble constituents from those insoluble in chloroform, and to prove the latter less well adapted to therapeutic use.

It is hoped to present soon a definite method for obtaining one or more active principles of digitalis, together with their chemical and pharmacologic properties. In particular, however, the writer's hope is to find a method by which the active agents can be separated and prepared for therapeutic use in pure form, unmixed with substances which interfere with their beneficial effects and with those which impair their stability.

HARDNESS OF SURFACE WATERS OF THE UNITED STATES[1,2]

By W. D. Collins
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Received September 2, 1920

This paper gives a very general account of the hardness of surface waters in the United States. The drainage basins as used in the studies of stream flow made by the United States Geological Survey are taken up in order, and an estimate is given of the range of the average quantity of dissolved mineral matter and of hardness likely to be found in river and lake waters. The same figures are shown in a table of the states arranged alphabetically. The numbers given should not be taken as absolute for any area. Exceptions can be found in all states, but over large areas the estimates given will be found to come very near the results obtained by analysis of the available river and lake waters.

In general, ground waters in any region contain more mineral matter in solution and are harder than the surface waters. A number of the larger cities obtain their supplies from distant sources which furnish water softer than that in nearer streams. Some cities soften their supplies, while others in order to avoid contamination use ground waters much harder than the surface water. These considerations affect the extension of the estimates given in this paper to cover city supplies in some localities.

SOURCES OF DATA

The United States Geological Survey has been collecting information in regard to the composition of river and lake waters for a number of years. The largest single project was a study of surface waters conducted from 1905 to 1908. Samples were collected daily at different stations and forwarded to laboratories for analysis. Composites of ten daily samples from a station were analyzed, making thirty-six analyses in a year. The results of this and similar work are reported in a series of Water Supply Papers of the United States Geological Survey.[3] A few analyses have been obtained from other sources.

EXPRESSION OF RESULTS

The values for dissolved solids represent in most cases the results obtained by evaporating a given quantity of water to dryness and weighing the residue after heating for one hour at 180° C. Hardness is expressed as calcium carbonate equivalent to the calcium and magnesium found by analysis. Results are given in parts per million.

DISSOLVED SOLIDS AND HARDNESS BY DRAINAGE BASINS

NORTH ATLANTIC SLOPE BASINS—Lake and river waters in the New England States rarely contain over 50 p. p. m. of dissolved solids. The hardness is generally equivalent to not more than 20 p. p. m. of calcium carbonate. Rivers draining the eastern part of New York, central and eastern Pennsylvania, New Jersey,

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[1] Published by permission of the Director of the U. S. Geological Survey.

[2] Presented before the Division of Water, Sewage and Sanitation at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

[3] Nos. 236, 237, 239, 273, 274, 339, and 363.

Delaware, Maryland, and northeastern Virginia have about 100 to 150 p. p. m. of dissolved solids, with hardness from 50 to 100 p. p. m.

SOUTH ATLANTIC AND EASTERN GULF OF MEXICO BASINS—Surface waters in the South Atlantic and eastern Gulf of Mexico basins have about 70 to 90 p. p. m. of dissolved solids, and hardness from 15 to 40 p. p. m. In Florida the waters are not so soft.

OHIO RIVER BASIN—River waters in western Pennsylvania are contaminated with mine drainage which at times makes the water acid. The dissolved solids and hardness may be around 100, and from 40 to 50, respectively.

Throughout Ohio and Indiana river waters carry 250 to 350 p. p. m. of dissolved solids, with hardness of 200 to 300.

Ohio River drainage in eastern and southern Illinois has about 150 to 200 p. p. m. of solids, with hardness around 100. Rivers emptying into the Ohio from West Virginia, Kentucky, and Tennessee have about 100 p. p. m. of solids, with hardness of 70.

ST. LAWRENCE RIVER BASIN—Dissolved solids increase in the Great Lakes from 60 p. p. m. in Lake Superior to 144 in the St. Lawrence River as it drains Lake Ontario. The hardness increases from 46 to 107. Drainage into the lakes from eastern New York is low in solids and hardness—80 and 45 p. p. m., respectively. The solids and hardness increase in western New York to nearly 200 and 150; in Ohio they are 300 and 200; and in Michigan about 250 and 200.

UPPER MISSISSIPPI RIVER AND HUDSON BAY BASINS—Wisconsin lake and river waters carry about 100 p. p. m. of solids with hardness of about 50. In northern Minnesota surface waters have 100 to 150 p. p. m. of solids and 70 to 100 parts of hardness. In the central and southeastern parts of the state more dissolved material is found, 250 to 300, and 200 to 250 p. p. m., respectively, of solids and hardness. The Mississippi River at Minneapolis has 200 and 157 p. p. m. of dissolved solids and hardness, respectively. Drainage from the western part of the state has much more solids and hardness, running up to 500 and 350 parts, respectively. Larger rivers in Iowa draining into the Mississippi have from 225 to 300 p. p. m. of solids, and hardness from 190 to 230. Rivers in Illinois have nearly 300 p. p. m. of solids, with 225 p. p. m. of hardness.

MISSOURI RIVER BASIN—Surface water in North and South Dakota may have not over 300 p. p. m. of dissolved solids and 200 p. p. m. hardness, but some large supplies have from 800 to 1000 p. p. m. solids and 500 to 600 p. p. m. hardness. Similar conditions prevail in Montana, Wyoming, and Nebraska.

Rivers in Kansas draining into the Missouri have from 350 to 550 p. p. m. solids and 225 to 350 p. p. m. hardness. Many of these rivers carry excessive quantities of sodium salts.

Over the greater part of Colorado surface waters contain from 300 to 700 p. p. m. of dissolved solids, with hardness from 200 to 400.

LOWER MISSISSIPPI RIVER BASIN—Waters in the drainage area of Arkansas River in Colorado, Kansas, Oklahoma, northeastern Texas, and Arkansas are very high in solids and hardness. A few rivers have less than 300 p. p. m. of solids and 200 p. p. m. hardness, but many have from 1000 to 3000 p. p. m. of dissolved solids and hardness from 500 to 1500.

Red River at Shreveport, La., carries 561 p. p. m. of dissolved solids with 255 p. p. m. hardness.

The Mississippi River has much less mineral matter in solution than the tributaries entering from the west. It carries from 200 to 300 p. p. m. of solids, with hardness of 125 to 175.

WESTERN GULF OF MEXICO BASINS—Drainage to the Gulf of Mexico from New Mexico and Texas is not very different from the Arkansas drainage. Some river waters are only moderately high in solids and hardness, but many have from 1000 to 3000 p. p. m. of solids, with hardness from 400 to 1500. Sodium salts are present in large amounts in these waters.

COLORADO RIVER BASIN—Small streams near the headwaters of rivers in the Colorado drainage basin may have soft water, but throughout Arizona and the parts of Utah, Colorado, and New Mexico in this drainage basin hard waters high in alkali abound. River waters may contain 500 to 700 p. p. m. of solids, with hardness of 200 to 300, and 100 to 150 p. p. m. of sodium.

GREAT BASIN—In Nevada and the parts of Oregon, Utah, and California draining into the Great Basin, rivers and lakes in the mountains may have dissolved solids and hardness as low as 100 to 200 and 30 to 100, respectively, but much of the surface water in this region is very high in solids—2000 to 30,000 p. p. m. Hardness is from zero to 200 or 300. Practically all the dissolved mineral matter in most of the lakes consists of alkali salts.

PACIFIC SLOPE BASINS IN CALIFORNIA—Rivers draining California to the Pacific Ocean contain from 80 to 1000 p. p. m. of dissolved solids with from 40 to 400 p. p. m. of hardness. The waters nearer the mountains are the softer, and in general those in the northern part of the state are softer than in the southern part.

NORTH PACIFIC SLOPE BASINS—Nearly all surface waters in Washington and Oregon have from 80 to 125 p. p. m. of dissolved solids, with 40 to 60 p. p. m. of hardness.

DISSOLVED SOLIDS AND HARDNESS BY STATES

The accompanying table gives approximate average results for dissolved solids and hardness of waters in each state. The waters of some states are very uniform in quality, but others show wide variations in different parts of the states. In the western states, streams and lakes in the mountains have soft water, while streams in valleys may carry large quantities of dissolved material. In areas of low rainfall large quantities of alkali salts are found in the river and lake waters.

SUMMARY

Soft surface water is found along the Atlantic, east Gulf of Mexico, and Pacific coasts, and along the northern boundary states. Hard water is found in

Dissolved Solids and Hardness of Surface Waters by States
(Parts per Million)

State	Dissolved solids	Hardness as $CaCO_3$ Equivalent to Ca and Mg	Notes
Alabama	70–90	15–40	.....
Arizona	500–700	200–300	100–150 Na
Arkansas	600	200	150 Na
California:			
Northern part	80–250	40–200	.....
Southern part	400–600	200–300	100 Na
Great Basin drainage	200–200,000	60–300–0	Higher concentrations practically all Na salts
Colorado	150–700	100–400	.....
Connecticut	50–100	25–50	.....
Delaware	80	40	.....
District of Columbia	100	40	.....
Florida	150	100	.....
Georgia	60–80	15–40	.....
Idaho	100–200	60–125	.....
Illinois	250–300	200–250	.....
Indiana	250–350	200–300	.....
Iowa	225–300	190–230	.....
Kansas:			
Drainage to Missouri River	350–550	225–350	High in Na salts
Drainage to Arkansas River	400, 1000–2000	250, 500–800	High in Na salts
Kentucky	100	70	.....
Louisiana	500	255	.....
Maine	20–50	5–20	.....
Maryland	100–150	50–75	.....
Massachusetts	50–60	15–25	.....
Michigan	250	200	.....
Minnesota:			
Northern	100–150	70–100	.....
Central and southern	250–500	200–350	.....
Mississippi	70–90	15–40	.....
Missouri	350	200	.....
Montana	300–600	200–300	.....
Nebraska	300–500	150–300	.....
Nevada:			
Mountainous area	100–200	30–100	.....
Lowland area	2000–30,000	200–300	High in Na salts
New Hampshire	20–50	5–20	.....
New Jersey	100–150	50–100	.....
New Mexico	500–3000	250–1500	.....
New York	100–150	50–100	.....
North Carolina	60–80	15–40	.....
North Dakota	300–800	200–600	.....
Ohio	250–350	200–300	.....
Oklahoma	1000–3000	500–1500	High Na
Oregon	80–125	40–60	.....
Pennsylvania	100–150	50–100	Acid waters at some places less in western part
Rhode Island	30–50	5–25	.....
South Carolina	70–90	15–40	.....
South Dakota	300–800	200–600	.....
Tennessee	100	70	.....
Texas	300, 1000–2000	200, 500–1500	High in Na
Utah	500–1000	200–300	100–250 Na
Vermont	30–50	5–25	.....
Virginia	70–90	15–40	.....
Washington	60–125	20–60	.....
West Virginia	100–150	70–100	.....
Wisconsin	100	50	.....
Wyoming:			
Mountainous area	200	150	.....
Lowland area	800–1000	500–600	.....

the middle-west states bordering the Mississippi and to the east. Hard and strongly alkaline water is found in the area outlined roughly by North Dakota, Arkansas, Louisiana, Texas, Arizona, and the southern part of California.

THE DETERMINATION OF ACETIC ACID IN PYROLIGNEOUS ACID

By V. E. Grotlisch

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Received July 17, 1920

In an investigation of the yields of various by-products obtained along with wood turpentine in the destructive distillation of certain resinous woods of western origin, carried out in the Bureau of Chemistry several years ago, it was found desirable to determine directly the percentage of acetic acid in the crude pyroligneous acid. This material, when obtained from highly resinous wood, such as the "fat" stump wood used in the commercial production of wood turpentine, contained considerably larger percentages of dissolved tars, phenols, and similar compounds than that obtained in hardwood distillation, as shown by the deep red color of the liquor and the dark brown acetate of lime obtained therefrom. Direct titration of the liquor with alkali was impracticable and impossible, as no end-point could be seen with any certainty, owing both to the color of the solution, even when much diluted, and also to the tars and phenolic bodies in solution. A search of the literature at that time failed to give a method which was directly applicable to such material.

Pickett[1] has recently described a method in which xylene was used to hasten the complete distillation of the acetic acid in the analysis of acetates by distillation from phosphoric acid. The use of xylene in the analysis of pyroligneous acid, for a somewhat different purpose, was suggested in 1915 by Mr. M. G. Donk, then of the Bureau of Chemistry, in correspondence between himself and the Bureau. The following method in its present form was evolved by the author and has been used in this laboratory since 1918. The xylene is used primarily to effect a partial separation of the acetic acid from the tars, phenols, and other impurities. The separation is not complete, however, so that in order to obtain really accurate results subsequent treatment of the distillate is necessary. This method thus has the advantage of giving a rapid, direct approximation of the quantity of acetic acid in a sample of pyroligneous acid, from which an accurate determination of the same can subsequently be obtained.

The following observations were the basis of the method:

(1) Xylene (b. p. 138° to 143° C.), which is immiscible with water, readily dissolves both the acetic acid and the impurities present in pyroligneous acid, but does not dissolve sodium acetate. The tars and phenols present are only slightly volatile at the temperature of boiling xylene, which is above the boiling points of acetic and propionic acids. Accordingly, if the xylene is present in large enough excess in a distillation mixture, the distillate at a certain point will contain all the acetic and propionic acids, with only a small proportion of the other bodies which interfere with the titration of the distillate, which gives a very close approximation of the quantity of acetic acid present.

(2) The tars, phenols, aldehydes, etc., which are present in pyroligneous acid are easily and completely oxidizable to carbon dioxide by alkaline potassium permanganate, which does not affect sodium acetate. Elimination of the products of the oxidation reaction leaves a pure solution of sodium acetate.

PROCEDURE

The following procedure has been adopted as the most convenient, rapid, and least liable to introduce errors: Place 120 cc. of xylene (which has previously been distilled from solid sodium hydroxide) in a 700-cc. long-neck, round-bottom flask, pipet in 10 cc. of the clear acid liquor, free from suspended tarry matter, and add a liberal quantity of finely broken pumice stone to prevent violent bumping during the distillation. Connect the flask to a 10-in. spiral glass condenser, clamped vertically or nearly so, and having an outflow tube about 8 in. long, by means of a tube such as is shown in Fig. 1, which prevents entrainment of unvaporized particles of xylene containing impurities. Cork stoppers must be used on account of the solvent action of xylene on rubber.

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[1] This Journal, **12** (1920), 570.

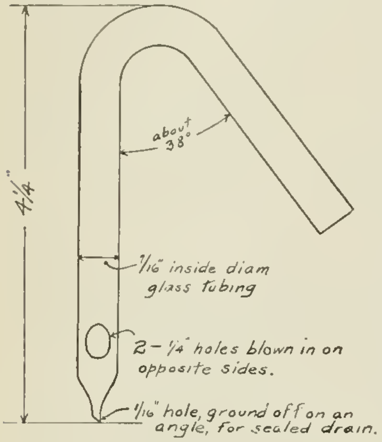
about 38°
4¼"
1/16" inside diam glass tubing
2 - ¼" holes blown in on opposite sides.
1/16" hole, ground off on an angle, for sealed drain.

FIG. 1

Distil slowly with a small flame at first, collecting the distillate in a 100-cc. graduated cylinder or Erlenmeyer flask, containing a few cc. of distilled water to seal the end of the condenser tube. After all water has been distilled over, increase the heat and continue distillation until the total distillate amounts to 75 cc., consisting of 10 cc. of an aqueous layer at the bottom and 65 cc. of xylene, which is colored a faint yellow by some impurities which have been carried over. It has been found that by the time 75 cc. of total distillate are obtained all acetic acid and the homologous formic and propionic acids have been distilled off. Further distillation continues to drive over acid bodies, which have in every case failed to give a test, on neutralization, for acetate, formate, or propionate, and are completely decomposed by potassium permanganate. No error in the final results will be introduced, however, if a little more distillate is collected.

A very delicate test for acetate[1] and the homologous salts (not for the free acid) is obtained by the use of a solution containing cupric chloride and sodium chloride. A solution containing 70 g. of the former and 50 g. of the latter per liter of distilled water gave very satisfactory results. It should be made up several days in advance and allowed to settle, decanting off the clear solution for use. If the fine, light green precipitate does not form at once, bring to a boil and allow to stand 10 min. One or two drops of 25 per cent acetic acid should clear up the solution. This reagent will detect one part of sodium acetate in 5000 parts of distilled water.

Wash the entire distillate into a 500-cc. Erlenmeyer flask and titrate to neutrality with 0.5 *N* sodium hydroxide, using about 10 drops of a solution of phenolphthalein in methyl alcohol as indicator. In case of over-titration titrate back with sulfuric acid. Toward the end of the titration the liquid must be well shaken after each addition of alkali to free the acid from solution in the xylene. This titration gives only a close approximation of the exact quantity of acetic acid present, as pointed out. The end-point is fairly sharp, but the pink color of the indicator fades quite rapidly, and the aqueous portion gradually turns brownish, due probably to absorption of oxygen by the phenolic bodies.

Now separate the aqueous portion from the xylene into a 400-cc. beaker, washing the xylene twice with a little distilled water. Boil down to about 70 cc., avoiding loss by spattering. Add 100 cc. distilled water and again boil down to 70 cc., and repeat this once more, to insure complete removal of all volatile esters, acetone, or other volatile bodies. After cooling, make alkaline with a few drops of sodium hydroxide solution, and add about 15 cc. of a strong solution of potassium permanganate. Cover with a watch glass and place on a steam bath for several hours, preventing evaporation to dryness by addition of water, if necessary. The permanganate oxidizes the organic impurities which cause the excess acidity, with the formation of a copious precipitate of manganese dioxide. The quantity of permanganate required will vary according to the nature of the original acid liquor. After standing on the steam bath for 3 hrs. there should still be enough undecomposed permanganate left to give the clear solution a distinct light purple color.

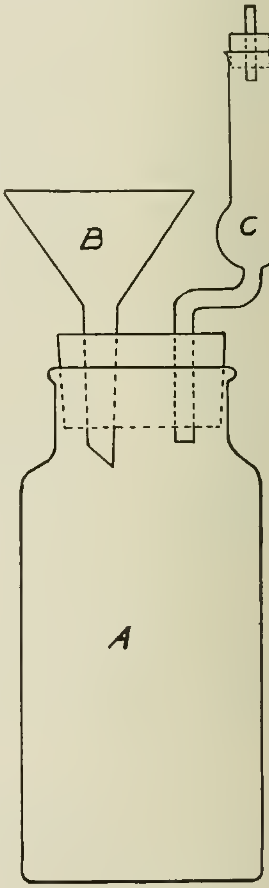

FIG. 2

A—8 oz., wide-mouth bottle. B—2 in. funnel. C—Small $CaCl_2$ tube charged with caustic soda and soda lime

Wash the solution and precipitate into a 300-cc., volumetric glass-stoppered flask, make up to mark, and thoroughly shake. Filter, with light suction, through a layer of washed asbestos on a Hirsch porcelain funnel, discarding the first 50 cc. of filtrate to insure that the collected portion is of the same concentration as the original volumetric solution. Pipet 200 cc. of the remaining filtrate into a beaker, and evaporate on a steam bath or over a low flame to about 75 cc. Cool to about 15° C. and acidify with a few drops of concentrated sulfuric acid. Add hydrogen peroxide, a few drops at a time with stirring, to destroy the permanganate. The solution is clear and colorless, and should still be slightly acid.

Add a slight excess of saturated barium hydroxide solution, to precipitate the sulfuric acid, the manganese, and the carbon dioxide formed through oxidation of the organic matter. An excess can be shown by adding a drop of sodium sulfate solution, when a white precipitate of barium sulfate will be formed in the clear supernatant liquid. Again evaporate to small volume on the steam bath, filter, and wash free from acetate with warm, previously boiled, distilled water, keeping air containing CO_2 away from the filtrate. The apparatus sketched in Fig. 2 was used for this purpose with satisfactory results. Before filtering, the bottle is filled with CO_2-free air by drawing air slowly through Tube C into the bottle. Wash the precipitate until the bottle is full, testing a final portion of the filtrate with the reagent described previously, to insure complete removal of acetate from the precipitate.

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[1] *J. Chem. Soc.*, **1873**, 577, or Prescott and Johnson, "Qualitative Chemical Analysis," 7th Ed., p. 258.

Wash the contents of the bottle into a 500-cc. round-bottom flask containing 10 cc. of sirupy, 85 per cent phosphoric acid (free from volatile acids), and add a few pieces of pumice. Distil off the acetic acid through the condenser used for the first distillation, sealing the end with a little distilled water, into a 500 cc. Erlenmeyer flask. When the volume of the liquid in the distillation flask has been reduced to about 45 cc. and the liquid begins to bump and froth, remove the flame and allow the flask to cool for a few minutes, taking care that the distillate does not suck back into the flask. Then add 25 cc. of warm distilled water, or the last washings in case acetate was still found in the filtrate after the bottle was full, and distil again to the same limit, repeating this operation twice more in order to insure complete removal of the acetic acid from the distilling flask.[1] Wash out the condenser into the receiving flask and titrate to neutrality. The quantity of standard sodium hydroxide used, multiplied by 1.5, represents the free acetic acid in the 10 cc. of acid liquor.

The xylene portions of the first distillate and also the residues from the first distillation may be collected, separately, for further use. They should be washed with a concentrated solution of sodium hydroxide and finally distilled over caustic soda.

EXPERIMENTAL RESULTS

In order to work out the above method and prove its reliability, various solutions containing acetic acid and acetates, as well as propionic acid, were made up, and different quantities of various organic substances, such as would probably be present in crude pyroligneous acid, were added, to give test solutions which might approach in their composition that of the pyroligneous acid, or at least contain some of the foreign bodies therein. These were analyzed, with the following results.

Expt. I—Ten-cc. portions of a number of different samples of crude pyroligneous acid were pipetted into 120-cc. portions of C. P. xylene and distilled as outlined above. The distillates were collected in fractions, as follows: first, a 50-cc. fraction, then in 5-cc. portions until a total of 90 cc. was collected. Titration of these fractions showed that all contained acid in diminishing quantity. Those collected after a total of 70 cc. had passed over failed in every case to give a test for acetate, after neutralization. On evaporation to dryness, brown, greasy residues were obtained, in which no crystals could be seen under a powerful magnifying glass. On distilling a 120-cc. portion of a composite xylene residue, obtained by combining the residues after 75 cc. of distillate were collected, with 10 cc. of distilled water as before, the distillate neutralized 1.0 cc. of 0.5 *N* sodium hydroxide, but gave no test for acetate.

Expt. II—Ten cc. of a dilute solution of acetic acid, equivalent to 16.24 cc. of 0.5 *N* sodium hydroxide (mean of three titrations), together with 60 cc. of freshly redistilled, neutral xylene, were added to 60 cc. of the xylene residue mentioned above, and distilled until a total of 75 cc. distillate had been collected. Titration required 16.96 cc. of the standard alkali, instead of the theoretical 16.24 cc. After separation of the aqueous portion and treatment with permanganate, as outlined, the final distillate from phosphoric acid of an aliquot equivalent to one-half the original quantity of acid used required 8.10 cc. of the standard alkali for neutralization. Theoretical, 8.12 cc.

Expt. III—Three solutions of sodium acetate, made by titrating 20-cc. portions of the same acetic acid (mean, 32.49 cc. alkali), were made up to 250 cc. in volumetric flasks. There were added, respectively, 4 cc., 5 cc., and 6 cc. each of methyl alcohol, acetone, and methyl acetate, and in addition a little pyrogallol to No. 2 and a little pyrocatechol to No. 3. Two 100-cc. portions, designated as *a* and *b*, were pipetted out and boiled down to about 40 cc., this being repeated. They were then treated with the permanganate, etc. The whole solution was kept for the final distillation, care being taken to wash the manganese dioxide precipitate until all traces of acetate and permanganate were recovered in the filtrate. Final distillation from phosphoric acid gave the following results, the theoretical quantity of sodium hydroxide required being two-fifths of 32.49 cc., or 13.00 cc.

Table I

Solution	NaOH Required for Final Titration Cc.	Difference from Theoretical Cc.
1*a*	13.10	+0.10
1*b*	13.14	+0.14
2*a*	13.03	+0.03
2*b*	12.92	—0.08
3*a*	13.05	+0.05
3*b*	12.95	—0.05

Expt. IV—Expt. II was repeated, several cc. each of methyl alcohol, acetone, and methyl acetate, and 0.25 g. each of pyrogallol and pyrocatechol being added to the distillation mixture. The first distillate required 16.80 cc. of 0.5 *N* alkali. After several boilings and oxidation with permanganate, the final distillate from phosphoric acid of an aliquot portion equivalent to one-half the quantity of acid taken neutralized 8.13 cc. of alkali.

Expt. V—The experiment was repeated, using in one case 3 cc. of beechwood creosote and in the other 15 g. of crystalline phenol. The first distillates required, respectively, 16.80 and 17.18 cc. of 0.5 *N* alkali. After treatment with permanganate, etc., the final distillates from aliquots equivalent to two-thirds of the quantity of acetic acid originally taken required 16.28 and 16.00 cc. of the alkali, proving that phenol and cresol are eliminated by the permanganate oxidation.

Expt. VI—A solution containing both acetic and propionic acid, in the ratio of 4 : 1, was used for the same test as Expt. II. Titration of 10-cc. portions of this acid required 25.72 and 25.80 cc. of sodium hydroxide; mean, 25.76 cc. The first distillates from the xylene, on 10-cc. portions of the acid, required, respectively, 26.02 and 26.20 cc. of sodium hydroxide. After oxidation with permanganate, etc., the final distillates from phosphoric acid on aliquots equivalent to two-thirds of the original acid taken neutralized, respectively, 17.05 and 17.25 cc. of the alkali. This proves that propionic acid is completely recovered in the method as outlined, and would be included in the final figures as acetic acid.

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[1] If any considerable number of determinations are to be made, the distillation procedure and apparatus described in Allen's "Commercial Organic Analysis," **1**, 4th Ed., 508, or in Sherman's "Organic Analysis," p. 130, can be advantageously used.

EXPT. VII—Table II shows the difference, in cc. of standard approximately 0.5 *N* sodium hydroxide used and the corresponding quantity of acetic acid indicated, between the first distillate with xylene and the final distillate from phosphoric acid, on 10-cc. samples of pyroligneous acid from various retort runs.

TABLE II

No.	NaOH Neutralized by First Distillate . Cc.	Quantity of Acetic Acid Indicated G. per Liter	NaOH Neutralized by Final Distillate Cc.	Actual Free Acetic Acid Present G. per Liter
1	22.55	70.81	21.58	67.76
2	22.30	70.02	20.60	64.69
3	23.35	73.32	21.60	67.82
4	23.05	72.38	20.84	65.44
5	26.96	84.65	24.70	77.56
6	18.96	59.53	16.60	52.12
7	20.95	65.78	18.06	56.71
8	24.35	76.46	22.64	71.09
9	23.25	73.00	20.74	65.12
10	17.10	53.70	13.36	41.95
11	16.74	52.56	15.40	48.36
12	20.40	64.06	18.44	57.90

CONCLUSIONS

The accurate determination of the free acetic acid in pyroligneous acid from pine-wood distillation cannot be made by a simple titration, owing to the fact that the liquor turns black on addition of alkali. and no end-point can be obtained, even when diluted 40 times. When it is distilled, directly or with steam, the same trouble is experienced with the distillate, on account of the large proportion of volatile phenolic bodies which pass over. A partial separation of the free acid from the impurities, affording a very close approximation of the free acetic acid present, can be made by distilling the acid liquor with xylene. Even then foreign bodies of an acid nature are present in the distillate, and in order to get accurate results these impurities must be removed by a subsequent treatment of the distillate. This can be done by oxidizing with potassium permanganate solution in the presence of a small excess of alkali, with subsequent removal of the oxidation products.

The close agreement between the results obtained in the experiments and the theoretical quantity of sodium hydroxide solution required shows that it is possible to remove any acetone or methyl acetate from the first distillate, before treating with permanganate, by boiling the solution down several times, and that the presence of pyrogallol or pyrocatechol, both of which, or bodies closely related thereto, may be present in pyroligneous acid, does not affect the final results. Richter's "Organic Chemistry" states that acetic acid is one of the products of the oxidation of pyrogallol in alkaline solution. If such is actually the case, the acid, or its salts, must be produced in extremely small quantities, as indicated by the results obtained in Expts. II and IV, and does not influence the final results. Formic acid is not included in the final results for acetic acid, since it is completely oxidized to carbon dioxide by the permanganate. Propionic acid would be unaffected, and included in the final figures calculated as acetic acid. Butyric acid would probably be held back by the xylene on account of its high boiling point.

THE DETERMINATION OF HYDROCHLORIC ACID AND NEUTRAL CHLORIDES IN LEATHER[1]

By Arthur W. Thomas and Alexander Frieden

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A method for the determination of sulfuric acid and neutral sulfates in leather has been offered by one of us.[2] Briefly, this method is carried out as follows:

One gram of leather is placed in a 250-cc. volumetric flask and covered with 200 cc. of a 0.1 *M* KH_2PO_4 (or NaH_2PO_4) solution. The flask is immersed in a bath of boiling water for 2 hrs. It is then cooled, made up to the mark with water, shaken well, and filtered through a folded paper. The first 20 to 25 cc. of filtrate are discarded, then 200 cc. of filtrate are collected, transferred to a 600-cc. beaker, 20 cc. of molar hydrochloric acid added, heated to boiling, and sulfate determined in the usual way by precipitation with barium ion. This procedure gives total sulfate. A second sample of leather is treated in a similar manner, except for the use of water instead of the phosphate solution, giving the neutral sulfate present. The difference between the two values obtained shows the amount of acid sulfate in the leather.

It was undertaken to apply the same principle to the quantitative removal from, and determination of neutral and acid chlorides in leather.

MATERIALS

E—Strap leather, vegetable tanned, treated with hydrochloric acid
H—Vegetable tanned leather, treated with hydrochloric acid
I—Vegetable tanned leather, treated with hydrochloric acid
J—Vegetable tanned leather, treated with sodium choride
K—Vegetable tanned leather, treated with sodium chloride
M—Chrome calf leather, treated with hydrochloric acid
N—Hide powder, tanned with chromic chloride

Leathers H, I, and M were prepared by soaking finished samples of the cut-up leathers in dilute hydrochloric acid, after which they were filtered, washed just enough to remove adhering acid solution, and dried. Leathers J and K were prepared in a similar manner, using sodium chloride instead of hydrochloric. acid.

EXPERIMENTAL PART

EXTRACTION WITH PHOSPHATE SOLUTION—Experiments were carried out to note the effect of different times of heating and of different weights of leathers on the extraction of total chlorides by the phosphate solution. The reason for trying different weights was due to the fact that in the case of sulfate extraction it was found that not more than 1 g. of leather containing more than 5 per cent SO_3 could be used, if a quantitative removal of the sulfates was to be accomplished by use of 200 cc. of the phosphate solution.

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[1] Presented before the Leather Chemistry Section at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

[2] A. W. Thomas, *J. Am. Leather Chem. Assoc.*, **15** (1920), 504.

As shown below, 2 hrs. were found sufficient time for the digestion and 1-g. samples not too large for quantitative results. Extraction times longer than 2 hrs. did not yield any more chloride than the 2-hr. extraction.

Leather N Grams	Chloride, Calculated as Cl, Extracted by 0.1 *M* KH_2PO_4 Solution in 1 Hr. Mg.	2 Hrs. Mg.
0.5	....	39.6
1.0	39.5	41.1
2.0	37.3	39.8

EXTRACTION WITH WATER—Since neutral sulfates are quantitatively extracted from leather by means of pure water in 2 hrs. at 100° C., this procedure was tried upon the samples of leather containing sodium chloride, with the following result:

LEATHER	Cl Found KH_2PO_4 Extraction Mg.	Cl Found Water Extraction Mg.
J	17.7	17.8
K	23.7	23.6

Hence, in the case of these leathers which contained neutral chloride only, all the chloride was extracted with water, because, as will be shown later, these yields are identical with those obtained by phosphate extraction which removes all chlorides quantitatively.

In the sulfuric acid method it was found that while all the neutral sulfate was removed by digestion in water, a small portion (7 to 10 per cent of the total) of the acid sulfate was hydrolyzed and extracted as well, and, therefore, the effect of water on the acid chloride was investigated with the result:

LEATHER	Total Acid Cl Present per Gram Mg.	Acid Cl per Gram Extracted by Water in 0.5-Hr. Digestion Mg.
H	19.9	19.5
M	28.1	16.9
N	40.1	17.1

It was obvious from these experiments, that the water extraction could not be used for separation of neutral chloride from acid chloride in leather. Sample H showed practically complete removal of the hydrochloric acid by water. This effect has been noted by us in other samples of vegetable tanned leathers which had been treated with hydrochloric acid, and we do not consider such prepared samples as proper material upon which to base a test. It appears that all of the hydrochloric acid does not combine chemically with finished vegetable tanned leathers, because it reacts with the same groups of the collagen molecule as tannins do. In the cases of chrome tanned samples, M and N, all the acid chloride was not extracted by water, but since the amount removed was so large, it was evident that the method which worked very well for sulfuric acid and neutral sulfate separation would have to be modified if separation of acid and neutral chloride was to be attained.

Since, in our opinion, acids are chemically combined with collagen, provided they come in contact with the collagen before all the reactive groups of the collagen are combined with tanning agents, the removal of an acid from leather by means of hot water is due to hydrolysis. It is evident then that collagen hydrochloride is much more readily hydrolyzed than collagen sulfate.

EXTRACTION WITH ALCOHOL—Since hydrolysis of the collagen-acid compound cannot take place in alcohol, while chlorides are soluble in this solvent, its efficacy for extraction of neutral chloride was studied. The 95 per cent ethyl alcohol was purified by distillation over alkali. The typical figures given below show that alcohol quantitatively removes neutral chloride from leather. The digestion was carried out at 75° C. for 2 hrs., although in many cases 1.5 hrs. were found to be sufficient.

LEATHER	Neutral Cl Present per Gram Sample Mg.	Cl Extracted by Alcohol per Gram Sample Mg.
J	17.8	17.9
K	23.7	23.6

The amounts of acid chloride extracted by alcohol after 2 hrs. digestion at 75° C. were as follows:

LEATHER	Acid Cl[1] Present per Gram Sample Mg.	Acid Cl[1] Extracted by Alcohol per Gram Sample Mg.
I	21.1	5.4
L	28.1	5.4
N	40.1	5.9

[1] While we call this "acid chloride," we have no means of knowing whether all is present as such. The leathers in the cases of I and L, and the hide substance in the case of N were treated with acid chloride solutions, but this treatment does not necessarily result in its all existing in the leather as acid chloride, since it is quite possible that some may have been converted to neutral chloride in the leather.

The above experiments indicated that while neutral chloride was quantitatively extracted by alcohol, a small amount of the acid chloride present was apparently extracted as well, but on account of the possibility that some of the chloride considered as acid chloride might have been converted to neutral chloride, and also since no method for the determination of hydrochloric acid in leather is available, we feel justified in offering this as a satisfactory method at the present time.

METHOD

TOTAL CHLORIDE—One gram of leather is placed in a 250-cc. volumetric flask and covered with 200 cc. of a 0.1 *M* solution of KH_2PO_4 or NaH_2PO_4. The flask is immersed in a bath of boiling water for 2 hrs., and shaken occasionally. The solution is then cooled, made up to the mark with water, shaken well, and filtered through a folded paper. The first 20 to 25 cc. of filtrate are discarded, then 200 cc. of the filtrate are collected in a volumetric flask, transferred to a 600-cc. beaker, and acidified by addition of 10 cc. of molar nitric acid which prevents precipitation of silver phosphate when the silver nitrate is added later. The solution is heated and 10 cc. of 0.1 *M* silver nitrate solution added. After the silver nitrate treatment, a further addition of 20 cc. of concentrated nitric acid (15 *M*) is made, and this mixture is evaporated in the dark to about 50 cc. volume, in order to oxidize and dissolve organic matter which has precipitated with and contaminated the silver chloride. The solution is then diluted with about 200 cc. of water, heated, and filtered through a Gooch crucible. The silver chloride is washed, dried, and weighed in the usual manner, and the total chloride in the leather is computed from the weight of silver chloride obtained.

ACID CHLORIDE—A second sample of 1 g. of leather is covered with 200 cc. of purified 95 per cent alcohol in a 250-cc. volumetric flask and digested at about 75° C. for 2 hrs., with occasional shaking. The contents of the flask are then cooled, made up to the mark with water, mixed and filtered *immediately.* (If made up to the mark with alcohol, there is no danger of hydrolysis of the collagen-acid compound, and hence *rapid* mixing and filtration are not required.) The first 20 to 25 cc. of filtrate are discarded, and 200 cc. of filtrate collected, transferred to a 600 cc. beaker, made just alkaline with sodium hydroxide, and the alcohol evaporated off (if it is desired to recover the alcohol, a flask may be used, but after the alcohol is removed, the residue should be washed into a beaker). Sufficient nitric acid is added to render the solution slightly acid. The solution is heated and 10 cc. of 0.1 *M* silver nitrate solution added. From this point the procedure is identical with that outlined above, after the addition of silver nitrate. From the silver chloride obtained here, the neutral chloride may be calculated, and this value subtracted from the total chloride value indicates the amount of acid chloride present in the leather.

RESULTS

The results obtained by this method were compared with the amounts of chloride obtained by the method of determination of total chloride by ashing the leather, previously soaked with sodium carbonate solution and covered with dry sodium carbonate. The ashing was conducted in a muffle furnace at as low a heat as possible, and the amount of chloride present in the sodium carbonate was determined, and correction applied in each case.

LEATHER	Total Cl Found by Ashing Per cent	Total Cl Found by Phosphate Digestion (1) Per cent	Neutral Cl Found by Alcohol Digestion (2) Per cent	Acid Cl Difference between (1) and (2) Per cent
N[1]	4.21	4.01	0.59	3.42
M[1]	2.80	2.81	0.54	2.27
I[1]	2.16	2.11	0.54	1.57
E[1]	1.23	1.21	....	....
J[2]	....	1.79	1.78	0.01[3]
K[2]	2.52	2.37	2.36	0.01[3]

[1] Presumably all chloride present was acid chloride.

[2] All chloride present was neutral chloride.

[3] Actually zero; the method is not accurate to this extent.

In general, the total chloride found by the method of ashing is greater than that found by the phosphate digestion. This is due to chlorine present as part of the protein molecule in the leather or in forms other than chloride.

An objection might be raised against the use of ethyl alcohol. There seems to be no reason, however, why denatured alcohol that has been twice distilled, first over phosphoric acid and then over alkali, would serve just as well as pure ethyl alcohol.

ACKNOWLEDGMENT

We take pleasure in acknowledging the generous support of Messrs. A. F. Gallun and Sons Company in this investigation.

SOME RESULTS OF THE DETERMINATION OF POTASH BY THE LINDO-GLADDING METHOD[1]

By **H. C. Moore and R. D. Caldwell**

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Fertilizer chemists and others experienced in the determination of potash in mixed fertilizers, various fertilizer materials, and potash salts by the official (A. O. A. C.) Lindo-Gladding method, have long known that the use of 80 per cent alcohol (ethyl) as prescribed by the official method gives lower results than when 95 per cent or stronger alcohol is used, as in the official methods of some other countries. This discrepancy has been attributed to the greater solubility of the potassium platinic chloride in the 80 per cent alcohol.

The writers found, however, that results obtained with 95 per cent alcohol were but slightly higher than those obtained with 80 per cent alcohol when using a sample of pure potassium chloride, but that the discrepancy was greater in case of a sample of potash salts containing chlorides and sulfates of sodium and other elements.

The preliminary data suggested the explanation that the sodium salts were more soluble in the 80 per cent alcohol than in 95 per cent, and that this alcoholic solution of sodium salts, rather than the 80 per cent alcohol alone, exerted a greater solvent action on the potassium platinic chloride. To test out this theory some further tests were undertaken. A sample of dried potassium chloride (Kahlbaum's) was weighed out and aliquot parts of this solution were taken, 1 cc. hydrochloric acid added, together with an excess of platinic chloride, and the solution evaporated to a thick paste. From this point on, the procedure varied only in the strength of alcohol used in washing. First, three washings were made by decantation with alcohol, five with Lindo-Gladding (ammonium chloride) solution, and finally, transferring the precipitate to a Gooch crucible with this solution, six times with alcohol. The crucible was dried and weighed, leached with boiling water, and again weighed, the difference giving the weight of potassium platinic chloride. The alcoholic washes[2] were as follows:

(1) 80 per cent alcohol for first three as well as last six washes
(2) 92 per cent alcohol for first three as well as last six washes
(3) 92 per cent alcohol for first three and 80 per cent for last six washes

The results of these experiments, in terms of per cent K_2O found, were as follows:

TABLE I

MATERIAL	80 Per cent Alcohol	92 Per cent Alcohol	92 Per cent Followed by 80 Per cent Alcohol
Without NaCl....................	63.24	63.52	63.08
Same as above, 0.2 g. NaCl added before evaporation............	62.82	63.22	63.18
Same as above, 0.4 g. NaCl added	62.82	63.22	63.24
Same as above, 0.4 g. NaCl added, double amount platinic chloride solution added................	62.82	.....	.....
Same as above, added 0.4 g. NaCl to KCl aliquots, added H_2SO_4, evaporated....................	62.14	63.44	63.16

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[1] Presented before the Fertilizer Division at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

[2] Using denatured alcohol, free from pyridine, and per cent by volume determined by specific gravity as determined from tables for ethyl alcohol.

The potassium chloride was not tested for purity but was assumed to be pure (theoretical K_2O, 63.17 per cent). Whether it was pure or not does not matter so much, as aliquots from the same stock solution were used in all of the above tests.

The results indicate that the presence of sodium chloride or sodium sulfate causes low results when using 80 per cent alcohol, and that when using 92 per cent alcohol the results are practically the same whether the sodium salts are present or not. Furthermore, the fact that results are practically the same with or without the sodium salts when washing first to remove the excess platinic chloride, then with Lindo-Gladding solution to remove sodium salts, and finally with 80 per cent alcohol, tends to prove our theory that the solution of sodium chloride or sulfate in 80 per cent alcohol does have a greater solvent action on the potassium platinic chloride than the 80 per cent alcohol alone.

As further proof another series of experiments was made. Pure potassium platinic chloride was prepared by evaporating the leachings from the crucibles in the above tests, washing thoroughly with 80 per cent alcohol, Lindo-Gladding solution, and finally with 80 per cent alcohol, and drying in an oven at 130° C. Four grams were dissolved and diluted to 500 cc., and aliquots of 25 cc. (equal to 0.2000 g.) were taken; a few drops of hydrochloric acid and of platinic chloride were added, together with sodium chloride and sodium sulfate as shown in Table II, and evaporated to paste as in regular potash determination. The washing was precisely the same as in the foregoing tests, except that 95 per cent alcohol replaced the 92 per cent alcohol used in the previous tests. Also, denatured alcohol, Formula 30, was used. The results shown in Table II, giving grams of K_2PtCl_6 found, are in every case the average of two or three determinations.

TABLE II

	80 Per cent Alcohol Grams	95 Per cent Alcohol Grams	95 Per cent Alcohol First, 80 Per cent Alcohol Last Grams
K_2PtCl_6 alone	0.1999	0.2009	0.2018
0.1 g. NaCl added	0.1992	0.2017	0.2007
0.2 g. NaCl added	0.1978	0.2025	0.2005
0.4 g. NaCl added	0.1960	0.2002	0.2002
0.1 g. Na_2SO_4 added	0.2011	0.2012	0.2013
0.2 g. Na_2SO_4 added	0.1988	0.2020	0.2009
0.4 g. Na_2SO_4 added	0.1985	0.2009	0.2007
0.05 g. NaCl + 0.05 g. Na_2SO_4 added	0.1995	0.2011	0.1999
0.1 g. NaCl + 0.1 g. Na_2SO_4 added	0.1983	0.2006	0.2009
0.2 g. NaCl + 0.2 g. Na_2SO_4 added	0.1957	0.2004	0.2012

In these results the sodium chloride causes slightly lower results than the sulfate. This condition is somewhat different from those in Table I, as in that case the potassium salt also was converted to sulfate, thus yielding some free sulfuric acid after evaporation, whereas in Table II no free sulfuric acid would be formed in any case. Otherwise these data confirm those in the first table.

No very complete study of the effect of various salts or the strength of the alcohol used in washing is covered by the results given above, but sufficient has been done to warrant the further careful study of this subject. The effect of other salts, such as those of calcium and magnesium, should be included. The data do seem to warrant the suggestion that the official method be changed at least to allow the use of the strong alcohol, about 95 per cent, for the first washings to remove excess platinic chloride, and the 80 per cent alcohol for final washing, if this is considered necessary; then if there is anything present which 80 per cent alcohol should remove and which 95 per cent alcohol will not remove, it can be done in the final washing without including the effect of sodium or other salts.

Unfortunately all analysts have not followed the official method in the use of 80 per cent alcohol. This includes some works laboratories as well as referees. Some use strong alcohol altogether, some Columbian spirits (about 96 per cent), while others have faithfully followed the official method in using 80 per cent alcohol as prescribed, thereby finding lower percentages of potash. While the results obtained by using stronger alcohol are nearer the true values, as judged from the foregoing at least, the fact remains that the official method specifies 80 per cent alcohol, and all laboratories making this determination should be governed accordingly until the method is changed.

Fertilizer chemists have been aware for some time that the results obtained on analyses of mixed fertilizers, even on carefully prepared laboratory samples, are lower than the results calculated from the analyses of the potash salts used. This has been largely attributed either to the formation of some insoluble potassium silicate or to the selective absorption of the calcium oxalate or phosphate precipitate for salts of potassium. How much is really due to either of these causes, and how much to the strength of the alcohol, is unknown, as 80 per cent alcohol has been used when making study of this problem.

Our own results have usually indicated a loss of from 2 per cent to 3 per cent of the potash as calculated, and this is no small item to the fertilizer manufacturer, who deserves credit for all of the potash added.

THE DETECTION OF OILS OTHER THAN LINSEED IN PAINTS BY MEANS OF THE HEXABROMIDE NUMBER OF THE FATTY ACIDS[1]

By Herbert Bailey and Walter D. Baldsiefen

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The abnormally high price of linseed oil during the last two years has naturally increased interest in methods for detecting adulteration of this basic paint material. Messrs. Steele and Washburn[2] in their recent article on "A New Hexabromide Method for Linseed Oil" have most ably covered the more important work on hexabromide methods. In using the modification of Eibner's method[3] proposed by Steele and Washburn, which was submitted for coöperative work to members of Committee D-1 of the

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[1] Presented in part before the Division of Agricultural and Food Chemistry at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

[2] THIS JOURNAL, **12** (1920), 52.

[3] *Farben-Ztg.*, Nov. 23, **1912** (No. 8).

A. S. T. M., the authors have felt that there was room for further simplification in the procedure. In the hope that under properly controlled conditions it would be possible to get concordant results without separating the fatty acids, *i. e.*, by brominating the glycerides, the procedure adopted by Bailey and Johnson in their work on salmon oil[1] was studied. A fairly complete investigation has proved, however, that it is necessary to add the bromine to the fatty acids in order to get results of any value in detecting the presence of foreign oils in linseed. In our method, therefore, we have adopted a procedure similar to that recommended by Steele and Washburn for the preparation of the fatty acids. As a solvent for the fatty acids we very much prefer ether to chloroform, as in the latter the hexabromides are quite soluble, and the chloroform must therefore be completely removed before they can be precipitated. Work of previous investigators, especially Sutcliffe,[2] has pretty conclusively demonstrated that under properly controlled conditions the hexabromides of the unsaturated fatty acids can be quantitatively separated from ether solutions. Another advantage which will appeal to the works chemist is that when ether is used it is unnecessary to prepare a special chloroform as in the Steele-Washburn method, and a slight excess of bromine does not affect the final results, so that it is not necessary to use amylene or other reagents to neutralize the excess added in the brominating process. It is essential, however, that an ether saturated with linseed oil hexabromides be employed, as they have a slight though appreciable solubility even at 0° C.

BROMINATING REAGENT

Bailey and Johnson found it much more convenient to add the bromine in acetic acid solution than as the pure element. Gemmell,[3] in his review of the work of earlier investigators on the insoluble bromine value of oils, pointed out that the amount of acetic acid present materially affects the weight of bromides obtained. Presumably there is some optimum mixture of ether and acetic acid which will be most satisfactory as the bromination solvent. Freyer and Weston[4] recommended 2 cc. of glacial acetic acid and 20 cc. of anhydrous ether. We found that when 20 cc. of ether and 4 cc. of acetic acid were used in a determination, our pure linseed oil gave hexabromide values of 42.8 and 44.4, while with 25 cc. of ether and the same amount of acid the results were 43.9 and 44.3. This indicated that not only more concordant results but also slightly higher values were obtained when the percentage of ether in the mixture was increased. As 1 g. of linseed oil fatty acids requires about 0.5 cc. of bromine to saturate them, and 30 cc. is a convenient volume in which to carry out the bromination, a 20 per cent (by volume) glacial acetic acid solution of bromine has been adopted as the brominating reagent, and 25 cc. of ether plus 2 cc. of acetic acid as the solvent in which to dissolve the fatty acids. This gives in the final solution of fatty acids, bromides, ether, and acetic acid, approximately 13 per cent of the acetic acid, or practically the same as recommended by Freyer and Weston.

BROMINATION PROCEDURE

EFFECT OF TEMPERATURE OF BROMINATION—In this work the temperature of the ether solution of fatty acid has been kept about —10° C. by immersion in a small bath of chopped ice and hydrochloric acid. In a series of determinations on two samples of mixed fatty acids two brominations of each were made at 0° C. and two at —10° C. Those at 0° C. gave values for Sample A of 35.1 and 37.9, and for B of 35.7 and 36.6, a variation in the first two of 2.8 and in the second 0.9. At —10° C. the hexabromide values were 36.3, 37.5 and 37.2, 37.6, respectively, showing a discrepancy of 1.2 on Sample A and only 0.4 on B. While the data obtained were too meager to warrant any very definite statement with reference to the effect of temperature on the bromination, they were sufficient to convince us that it is safer to work at —10° C. than at 0° C.

EFFECT OF RATE OF BROMINATION—Many previous investigators have mentioned the importance of allowing sufficient time after the addition of the bromine to the fatty acids for complete precipitation of the hexabromides, but little attention has been paid to the rate at which the brominating reagent is added. Although Bailey and Johnson had confirmed the statement of Sutcliffe that the best results were obtained by allowing the brominated mixture to stand over night, we made one series of determinations in which this point was investigated. It was found that the same fatty acids precipitated in the same way gave values of 39.7 if filtered and washed after standing 3 hrs., 40.7 after 6 hrs., and 43.0 when allowed to stand over night (16 hrs.) in the ice box. Apparently there is a continued increase in the formation of ether-insoluble bromides with increased time of standing, but this we believe is not due to the substitution of bromine in the chain, as only a trace of free hydrobromic acid could be detected even in the solution which had stood over night.

Experiments in which the same linseed oil acids were treated with the same amount of the acetic acid solution of bromine under identical conditions, with the exception of the rate at which the bromine reagent was added, proved that this has some effect upon the yield of brominated products. Using 4 cc. of the reagent, a rather large excess, in each case, when the addition took place in 3 min., the hexabromide value found was 43.9, in 10 min. 46.9, and in 30 min. 48.2. Another sample of fatty acids was treated with 2.7 cc. of the bromine reagent (which was just sufficient to give a slight excess of bromine as shown by the permanent yellow color), and the rate of addition had much less effect on the final results. Pouring in the entire 2.7 cc. of solution all at once, we obtained 43.1 and 43.2 as the hexabromide values, and when the reagent was dropped in slowly from a buret during the course of 10 min., the values were 44.8 and 44.9. In both sets of experiments the brominated solutions were allowed to stand over night in the ice chest before filtering and washing.

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[1] This Journal, **10** (1918), 999.

[2] *The Analyst*, **39** (1914), 28.

[3] *Ibid.*, **39** (1914), 297.

[4] "Technical Handbook of Oils, Fats and Waxes," Cambridge, **2** (1918), 111.

DETAILED DESCRIPTION OF METHOD

REAGENTS—The following reagents in about the quantities mentioned will be required for making ten determinations:

Sodium Hydroxide Solution (1.4 sp. gr.)—Dissolve 75 g. of C. P. NaOH in water and make up to 200 cc.

Alcohol (95 per cent by volume)—200 cc. (denatured alcohol is satisfactory).

Hydrochloric Acid—C. P., concentrated, 300 cc.

Glacial Acetic Acid—20 cc. This acid should not show any reduction in the usual bichromate or permanganate tests.

Glacial Acetic Acid Solution of Bromine—30 cc. Five cc. of bromine + 25 cc. of acetic acid. The bromine must be free from non-volatile matter.

Ether Saturated at 0° C. with Linseed Oil Hexabromides—Wash in a separatory funnel a liter of laboratory ethyl ether with four successive 100-cc. portions of distilled water (ice-cold) and dry with fused calcium chloride over night. In the morning, pour the ether off through a folded filter paper into a 1.5- or 2-liter flask. Add several thin slices of sodium, reflux until there is no longer any evidence of the liberation of hydrogen, then distil off the dry ether.

Before the ether can be used it must be saturated at 0° C. with the hexabromides of linseed oil fatty acids to prevent its dissolving hexabromides during the washing of the bromination products in the determination. To prepare the hexabromides for this purpose, the directions given below have been found very satisfactory:

In a centrifuge tube dissolve about 5 g. of the fatty acids in 25 cc. of ether. Place the tube in a freezing mixture and add slowly, with shaking, bromine solution, until a red color is permanent. Let stand for at least 15 min., whirl the tube in a centrifuge until the precipitate has settled, and then pour off the ether. Rub up the precipitate with 20 cc. of cold absolute ether, whirl in a centrifuge, and pour off the wash ether. Repeat the washing with three more 20-cc. portions of ether. After drying, the hexabromide so obtained is pure enough for the preparation of the wash ether.

To saturate the dry ether with the hexabromides thus prepared or those from previous determinations made of pure linseed oils, which should always be saved, add at least 3 g. of the finely powdered substance and allow the solution to stand at room temperature with frequent shaking for several hours. Cool in ice water for 2 hrs., shaking from time to time, and finally filter as rapidly as possible into a dry cork-stoppered bottle.

APPARATUS—In addition to the ordinary equipment of a chemical laboratory, it is essential for the proper handling of this method that one have the following apparatus:

(*a*) Twelve centrifuge tubes about 1 × 5 in., of well-annealed heavy glass.

(*b*) A laboratory centrifuge with cups for holding the above centrifuge tubes.

DETERMINATION. *Preparation of the Fatty Acids*—To 50 cc. of oil in a 2-liter, round-bottom flask, add 40 cc. of NaOH solution (sp. gr. 1.4 = 36.50 per cent NaOH) and 40 cc. of alcohol. Close the flask with a 2-hole rubber stopper, carrying a quarter-inch tube, the lower end of which is just above the surface of the liquid, and heat on the steam bath for about 0.5 hr. Add a liter of hot distilled water and boil the soap solution until the alcohol is removed, passing a stream of CO_2 continually through the inlet tube. If a free flame is used, about 0.5 hr. boiling will be sufficient, but in this case it may be necessary to insert capillary tubes to prevent bumping of the liquid. If the solution is heated on the steam bath, 2 to 3 hrs. are usually required. After removing the alcohol, cool slightly, acidify with dilute HCl (1 : 1), and warm until the fatty acids form a clear layer (continuing to pass CO_2 through the system all the time). Transfer the fatty acids and part of the solution to a 500-cc. separatory funnel, allow to stand a few minutes until the fatty acids collect on top of the aqueous portion, and draw this off. Pour the remainder of the mixture from the flask into the funnel, and run off the aqueous portion. Add 300 cc. of hot water, shake vigorously, allow the fatty acids to separate, and again draw off the aqueous portion. Repeat this process until the wash water is neutral to methyl orange, three washings usually being sufficient. Run the warm fatty acids at once into a centrifuge tube and whirl for about a minute to separate the remaining water, then filter through a folded filter paper into a small bottle. When the major portion of the acids have run through the filter, discard the remainder, and stopper the bottle with a tight cork. It is obvious that the acids must be hot enough when poured on the filter to remain completely liquid until filtered, as otherwise some of those with a high melting point may separate.

Precipitation of the Hexabromides—Weigh accurately one of the centrifuge tubes, pipet into it as nearly as practicable 1.00 g. of the prepared fatty acids and again weigh. For transferring the fatty acid, a piece of 5 mm. glass tubing about 20 cm. long, drawn out to a tip and bent down at the lower end and up at the other in a shape similar to a "S" wrench, is convenient. To the fatty acids in the centrifuge tube add 25 cc. of the ether saturated with hexabromides and 2 cc. of glacial acetic acid. Cool the tube and its contents to about —10° C. by immersion in a bath of chopped ice to which a little commercial hydrochloric acid has been added; then, keeping the tube in the cooling mixture, add from a buret the bromine reagent at the rate of one or two drops per second, shaking the tube after each addition. Continue the bromination until the solution of fatty acids becomes permanently orange in color (usually for pure linseed oil this requires about 2.5 cc.), then remove the tube from the bath, stopper it with a cork, and allow to stand over night in an ice box.

Washing and Weighing of the Hexabromides—Next morning cool the tube by immersion in a bath of cracked ice and rub up the precipitate by means of a weighed glass rod, being sure to loosen any material adhering to the side of the tube. Whirl the tube in a centrifuge till the precipitate forms a hard cake on the bottom, cool in the ice bath, and decant the ether. Add 20 cc. of the wash ether previously cooled to 0° C. and rub up the precipitate with the glass rod. Return the tube to the ice bath and when cool remove and whirl again in the centrifuge. Cool once more and then remove the ether by decantation. Repeat this washing twice more, and after the last washing incline the tube and carefully tap it to spread the hexabromide precipitate part way up the sides. Warm the tube in water at 60° C. until most of the ether has evaporated, then attach it for 15 min. to a vacuum line showing a pressure of 30 to 40 mm., keeping the temperature around 60° C. Wipe the tube dry and allow it to stand in the balance at least 15 min. before weighing. To the weight of the precipitate in the tube add the weight of the slight amount adhering to the glass rod. This total weight of precipitate, multiplied by 100 and divided by the weight of the fatty acids taken, gives the hexabromide percentage.

RESULTS OBTAINED ON PURE LINSEED AND OTHER OILS

PURE LINSEED OILS—Unfortunately only a very few samples of pure linseed oil were available for this work, but these were analyzed, with the results given in Table I.

TABLE I—IODINE AND HEXABROMIDE VALUES OF PURE LINSEED OILS

Sample Number	535	553	563	564	648	801	813
Iodine No. (Hanus)	189.8	176.2	185.4	176.5	177.7	...	182.5
Hexabromide Value	44.1	42.6	42.1	42.3	43.0	41.1	42.9
	44.0	41.9	42.0	43.0	42.7	41.1	42.6
	...	...	...	...	43.2	...	...
	...	...	...	...	43.5	...	...
	...	...	...	...	42.6	...	...
	...	...	...	...	43.3	...	...

No. 535—Oil extracted in laboratory from Argentine seed
No. 553—Oil extracted with gasoline on commercial scale from North American seed
No. 563—Commercial raw oil
No. 564—Commercial acid refined oil
No. 648—Pure raw oil (authentic A.S.T.M. sample)
No. 801—Oil extracted in laboratory from Argentine seed
No. 813—Commercial raw oil

The figures in Table I are of interest, because they demonstrate, to a limited extent, it is true, the value of the hexabromide number as a basis for judging the purity of linseed oil. The iodine values of the oils examined vary from 176 to 189, 13 points, while the maximum difference in the hexabromide values is 3, from 41.1 to 44.1. This narrow spread in these so-called "constants" is, of itself, perhaps insufficient to warrant the substitution of the more difficultly obtained hexabromide value for the now almost universally accepted iodine value, but when considered with the values of these same constants for the oils commonly used to adulterate linseed oil it is of great importance. Discussion of this point will be taken up after Tables II and III, which give our results on treated linseed oils, soy-bean, fish and tung oils, have been considered. That the method which has been proposed for determining the hexabromide value is capable of giving results agreeing among themselves within about 2 per cent, is evidenced by the figures obtained on Sample 648.

TREATED LINSEED OILS—It is one thing to detect adulteration of pure raw linseed oils and quite another to determine the purity of "boiled," "heavy bodied," or "bung-hole boiled" oils. To ascertain the effect on the hexabromide value of the various treatments to which linseed oils are subjected in the preparation of commercial products, such as varnish and lithographic oils, we analyzed a number of samples representative of these classes. The results are shown in Table II.

TABLE II—IODINE AND HEXABROMIDE VALUES OF TREATED LINSEED OILS

Sample Number	Material	Iodine Number	Hexabromide Number
641	Linseed No. 553 + 5% Japan Drier[1]	166.8	41.1 42.6
642	Linseed No. 553 + 10% Japan Drier	161.5	41.0 40.9
643	Linseed No. 553 + 20% Japan Drier	152,5	39.2 39.0
644	Linseed No. 553 + 5% C.W.O. Drier[2]	164.8	40.8 39.2
645	Linseed No. 553 + 10% C.W.O. Drier	158.9	39.9 40.3
646	Linseed No. 553 + 20% C.W.O. Drier	147.4	39.9 39.4
561	Commercial Boiled Linseed	173.8	42.6 41.9
359	Heavy Bodied Linseed (Held at 560° F. for 5 brs.)	80.8	10.0

[1] 23% refined linseed oil, 5% litharge, 1% MnO_2, 71% turpentine substitute.

[2] 13% C.W.O., 8% rosin, 10% linseed oil, 5% lead + manganese salts, 64% turpentine substitute.

The Japan drier used in Samples 641 to 643 was really a mixing varnish and very evidently did not have any appreciable influence on the linseed oil with which it was mixed, other than mere dilution. Even after standing for three months these oils had not changed appreciably in their hexabromide values. Samples 644 to 646, which contained the China wood oil drier, were similarly unaffected, although their iodine numbers were reduced more than in the case of the first series.

So far we have had time to test only one true boiled oil, that is, a linseed oil to which had been added a small amount of lead and manganese in the form of their fatty acid soaps by heating the mixture at 250° F. until homogeneous. In this instance, Sample 561, neither the iodine nor hexabromide value differed from that for a pure raw oil. That the oxidation which takes place in bodying an oil very materially affects both the iodine and hexabromide values, as would be expected, is indicated by the results on Sample 359. The best commercial practice for the production of "boiled oil" does not involve any appreciable heating, as the metallic driers are nowadays usually fatty acid soaps, and, therefore, readily soluble in the oil. The older method for making boiled oils, which necessitated prolonged heating of the raw oil above 400° F. with an oxide or other inorganic salt of the metal, often caused not only a darkening of the oil, but an appreciable lowering of its iodine value. Where this older process is used, we have found that there is a decrease in the hexabromide value along with the iodine value.

There is some indication that the changes taking place in linseed oil during oxidation with air at high temperatures (400° F.) do not affect the hexabromide value and iodine value to the same extent. Some preliminary work makes it appear possible that, by determining both of these constants and getting the relation between them, a factor may be found which will make practicable the differentiation between pure oxidized or heavy-bodied linseed oils and mixtures of these with other oils.

OILS OTHER THAN PURE LINSEED—The most common substitutes for linseed are soy bean, fish, and (in a sense) tung, although the last at the present time is used to supplement rather than replace linseed. In Table III will be found the hexabromide values of a few samples of these oils and mixtures of soy-bean and linseed oils.

Table III—Iodine and Hexabromide Values of Oils other than Pure Linseed

Sample Number	Material	Iodine Number	Hexabromide Number
310	Commercial Raw Soy-bean Oil	133.2	4.2 4.9
658	Authentic Raw Soy-bean Oil	...	7.3 7.5
659	Authentic Raw Soy-bean Oil	...	5.7 5.5
660	Authentic Raw Soy-bean Oil	...	4.4 4.3
661	Authentic Raw Soy-bean Oil	...	4.3 4.3
812	Commercial Raw Soy-bean Oil	135.5	7.2
649	85% Linseed + 15% Soy-bean Oil	171.9	37.7 37.8
650	75% Linseed + 25% Soy-bean Oil	168.0	34.2 33.8
651	65% Linseed + 35% Soy-bean Oil	164.2	31.4 30.9
652	50% Linseed + 50% Soy-bean Oil	...	23.3 24.3
622	Pure Tung Oil	...	00.0
623	Menhaden Oil	...	35.9 36.2

By our method, the hexabromide value of pure soybean oil averages about 6.0, varying from 4.2 to 7.5, tung oil gives no ether-insoluble bromine derivatives, and fish oils yield octobromides which are insoluble in warm chloroform, and, therefore, readily distinguishable from the hexabromides. The melting point of the linseed hexabromides is about 180° C., while the fish-oil octobromides decompose at 200° C. without melting. It is well, therefore, to test the bromides after the final weighing by warming them gently. If they blacken, indicating the presence of fish oil octobromides, they may then be treated with hot chloroform which will dissolve all the hexabromides, leaving the insoluble octobromides which can be weighed. The details of this procedure have not been worked out, but anyone having occasion to make the separation can undoubtedly develop a method with little difficulty.

QUANTITATIVE APPLICATION OF THE METHOD—Using the figures given in Table III for Samples 649 to 652, which were of known composition, and the average hexabromide values of 42.0 and 6.0 for linseed and soy-bean oils, respectively, it is interesting to note the nearness with which the actual proportions of the two oils may be calculated. For Sample 649, taking the average value of 37.75, we get 88.2 per cent linseed and 11.8 per cent soy-bean oil, against 85 and 15 per cent actually present. Similarly for Sample 650, the proportions found are 77.7 per cent linseed and 22.3 per cent soy-bean, present 75 and 25 per cent; found for Sample 651, 69.8 per cent linseed and 30.2 per cent soy-bean, present 65 and 35 per cent; and in Sample 652, which contained equal parts of the two oils, we found 49.4 per cent linseed and 50.6 per cent soy-bean oil.

HEXABROMIDE VALUE OF OILS FROM COMMERCIAL PAINTS

The crucial test of the real value of the hexabromide method is in its application to the analyses of commercial paints. We have shown that the addition of substitutes to linseed oils cannot only be detected with a fair degree of accuracy, but also quantitatively determined, and the next question is how far this method is reliable with ordinary paints. Work on this phase of the subject has been started, but much more is needed before definite conclusions can be drawn with reference to the effect of various pigments, Japan driers, and other normal paint ingredients. In Table IV are collected the results obtained on a few paste colors, and paints of known and unknown composition.

Table IV—Analyses of Gasoline Extracts of Paste Colors and Paints

Sample Number	Hexabromide Value	Unsaponifiable Matter	Linseed Oil = 42 Calculated	Present	Soy-bean Oil = 6 Calculated	Present
761	37.7	0.96	88.0	...	12.0	...
762	29.2	0.38	64.4	...	35.6	...
763	21.7	0.38	43.6	...	56.4	...
764	18.5	0.66	34.7	...	65.3	...
765	35.4	0.90	81.6	...	18.4	...
766	41.4[1]	5.38	98.3	...	1.7	...
767	41.6	1.32	98.9	...	1.1	...
768	43.7	0.59	100.0	...	0.0	...
769	43.5	0.47	100.0	...	0.0	...
770	39.1	1.11	91.9	...	8.1	...
771	41.8[1]	3.40	99.4	...	0.6	...
772	3.0	...	0.0	...	100.0	...
788	30.5	1.63	68.0	...	32.0	...
789	25.3	1.80	53.6	...	46.4	...
790	28.6	1.20	62.8	...	37.2	...
791	27.0	0.46	58.3	...	41.7	...
792	24.0[1]	3.11	50.0	...	50.0	...
793	26.2	0.58	56.1	60.5	43.9	39.5
794	33.4[1]	3.56	76.1	76.2	23.9	23.8
795	39.6[1]	3.47	93.3	91.9	6.7	8.1
806	41.1	...	97.5	100.0	2.5	0.0
807	40.7	...	96.4	100.0	3.6	0.0
808	39.8	...	93.9	100.0	6.1	0.0
809	35.0	...	80.5	75.0	19.5	25.0
810	33.5	...	76.4	75.0	23.6	25.0
811	34.8	...	80.0	75.0	20.0	25.0
815	36.0	...	83.3	...	16.7	...
816	38.0	...	88.9	...	11.1	...
817	33.1	...	75.3	...	24.7	...
818	40.4	...	95.5	...	4.5	...
819	40.0	...	94.4	...	5.6	...
820	39.8	...	93.8	...	6.2	...
821	43.3	...	100.0	...	0.0	...
822	23.4	...	48.3	...	51.7	...
823	39.9	...	94.1	...	5.9	...

[1] Hexabromide value has been corrected for unsaponifiable in excess of 1.5 per cent.

The figures given in Columns 4 and 6 are calculated from the hexabromide values found, on the assumption that the average linseed hexabromide value is 42, that of soy bean 6, and that of the unsaponifiable zero. The normal content of unsaponifiable matter in linseed oil is about 1.0 per cent, and where not over 1.5 per cent was found in the fatty acids taken for analysis, we have assumed that only saponifiable oils were present in the original paint, and, therefore, applied no correction in these cases. In view of the limited amount of data which has been collected on this part of our investigation, we are hardly warranted in drawing any more than the general conclusion that Samples 761 to 765, 772, 788 to 795, and 809 to 817, all of which have a corrected hexabromide value of 39 or less, undoubtedly contain oils other than pure raw linseed.

Some idea of the degree of accuracy with which the relative proportions of linseed and soy-bean oils can be determined by the proposed method may be obtained from the results on paint samples of known composition, reported in Table IV. These Samples 793 to 811 were made in a small paint mill, and duplicate as nearly as possible commercial colors found on the market. The tabulated results indicate that it is possible by the hexabromide value to determine within about 10 per cent the amount of soy-bean oil which has been mixed with linseed in a paint, provided only these two oils are present in the saponifiable portion of the vehicle.

SUMMARY

(1) A method has been developed for the detection of substitutes in linseed oil and paints, based upon the determination of the amount of ether-insoluble hexabromides obtained by brominating the fatty acids under fixed conditions.

(2) This method is less complicated than some of those previously proposed, and gives more concordant results than the older methods.

(3) The hexabromide value of pure extracted or expressed linseed oils varies between comparatively narrow limits, and is, on the average, about 42.

(4) The average hexabromide value of pure soy-bean oil is 6, of tung and fish oils 0.0. The latter, however, gives ether-insoluble octobromides which can be readily separated from the hexabromides of the vegetable oils because of their insolubility in warm chloroform.

(5) The proportion of linseed oil in a mixture of this oil with soy-bean, tung, or fish oils, can be determined much more closely by means of the hexabromide than by the iodine value of that mixture.

(6) It appears probable that by the method developed a close approximation of the composition of the non-volatile vehicle of a paint may be obtained, but further study of the applicability of this hexabromide method to paint analysis is desirable.

NAPHTHALENE SULFONIC ACIDS. III—AN ALTERNATIVE METHOD FOR THE QUALITATIVE DETECTION OF NAPHTHALENE-2,7- AND 1,6-DISULFONIC ACIDS[1]

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In the second paper of this series by Ambler and Wherry[2] the qualitative detection of the 2,7- and 1,6-disulfonic acids is made by means of a microscopic examination of their β-naphthylamine salts after the other common naphthalene-sulfonic acids have been removed. While this microscopic examination is to be preferred, another method of detecting these two acids may be used as a confirmatory test, or in case a microscopic examination cannot be made conveniently.

The analysis is carried out exactly as in the former method up to the point where the mixed β-naphthylamine salts of the 2,7- and 1,6-acids are submitted to microscopic examination. That is, all the naphthalene-β-, 1,5-, 2,6-, and α-sulfonic acids have been removed. The salts from the acetone extraction are dried at 100° and then treated by the following method:

TEST FOR NAPHTHALENE-2,7-DISULFONIC ACID

A portion of the acetone-insoluble dry salts is boiled with 4 or 5 cc. of a mixture of four volumes of 95 per cent alcohol and one volume of water. Complete solution should take place, but if this does not occur, the insoluble material[1] is removed by filtering. On cooling the alcoholic solution, the β-naphthylamine salt of the 2,7-disulfonic acid crystallizes out.

TEST FOR NAPHTHALENE-1,6-DISULFONIC ACID

The remaining dry salts are covered with water, heated to boiling, and the β-naphthylamine removed by titrating with normal sodium hydroxide solution, using phenolphthalein as indicator. The volume of alkali used is noted. The amine is filtered off after cooling the solution, and the filtrate evaporated to dryness. The dry sodium salts are taken up in twice as much water as the normal alkali used in freeing the amine. To a measured volume of this solution, an exactly equal volume of concentrated sulfuric acid (sp. gr. 1.84) is added. The solution is cooled and crystal formation induced by rubbing with a stirring rod. The solution is allowed to stand for several hours with frequent rubbing and agitation before a negative result is assured. Under these conditions, the 1,6-disulfonic acid gives a crystalline precipitate of the sodium salt, which sometimes forms slowly, while the 2,7-acid remains in solution.

DISCUSSION

In the test for the 2,7-disulfonic acid, the β-naphthylamine salts of all the preceding acids will crystallize from the dilute alcohol. Hence the necessity of the complete removal of those acids. Further, the salt of the 1,6-disulfonic acid may crystallize out, if too large a quantity of the dry salts is used. A little practice with the pure salts, however, will give the analyst the necessary skill in manipulation and interpretation of results.

The test for the 1,6-disulfonic acid is delicate to about 16 parts per thousand. The directions make approximately an 8 per cent solution of the mixed salts. Hence, mixtures of the two acids which contain more than one part of the 1,6-acid to five parts of 2,7-acid, may be tested safely by this method; and if the 2,7-isomer is partially removed with diluted alcohol, mixtures containing even a smaller proportion of the 1,6-acid may be tested. The 2,7-isomer does not precipitate unless the solution contains about 10 per cent of the 2,7-salt. Since the directions for the test for the 1,6-acid are such that an approximately 8 per cent solution of the sodium salts is obtained, there is no danger of the 2,7-acid being precipitated instead of the 1,6-acid.

These relations are shown more clearly in the accompanying table. These results were obtained by taking 5-cc. samples of solutions of the two salts of the concentrations noted, and adding one cc. of concentrated sulfuric acid, sp. gr. 1.84, allowing the mixture to cool, and giving it plenty of time to crystallize. A second cc. of sulfuric acid was then added, and the experiment repeated. This process was repeated until 5 cc. of acid had been added. The table shows the result after the addition of the fifth cc. of acid.

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[1] Presented before the Division of Dye Chemistry at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

[2] This Journal, 12 (1920), 1085.

[1] β-Naphthylamine naphthalene-2,6-disulfonate, which crystallizes from the boiling solution upon cooling and is only slightly soluble in this reagent.

Table I—Results of Adding Equal Volumes of Concentrated Sulfuric Acid to Solutions of Naphthalene-1,6- and 2,7-Disulfonic Acids

Concentration of Salt Solution Used G. per 100 cc.	1,6-Acid	2,7-Acid
1.63	Turbidity	No precipitate
3.22	Crystals	No precipitate
6.44	Crystals	No precipitate
12.88	Crystals	Crystals[1]

[1] The mixture showed an immediate slight turbidity. On standing for 40 hrs. there was formed a heavy, silky, crystalline product.

SUMMARY

An alternative method of detecting naphthalene-2,7- and 1,6-disulfonic acids is given, which does not depend upon the use of the microscope.

THE INFLUENCE OF POTASSIUM PERMANGANATE ON KJELDAHL NITROGEN DETERMINATIONS

By **Donald C. Cochrane**

Institute of Animal Nutrition, Pennsylvania State College, State College, Pa.

Received August 17, 1920

In a paper read before the Association of Official Agricultural Chemists at the meeting of November 1915, Frear questioned the accuracy of the Kjeldahl method for nitrogen as commonly used in fertilizer analysis. The data which Frear presented showed that a large loss of nitrogen occurred in determinations on fertilizers when potassium permanganate was added; that the time elapsing between cessation of boiling and the addition of the permanganate influenced the results; and that the presence or absence of nitrates made no appreciable difference in the loss occurring on the addition of the permanganate.

It was therefore deemed advisable to check the method upon substances commonly met with in nutrition work, paying particular attention to the influence on the results of the addition or non-addition of potassium permanganate.

TECHNIQUE

METHOD 1. WITH POTASSIUM PERMANGANATE—Weigh by difference from a glass-stoppered weighing bottle directly into a 300-cc. Kjeldahl digestion flask about 1 g. of substance, and add 0.3 g. of metallic mercury and 30 cc. of concentrated sulfuric acid, rotating the flask during the addition of the acid in order to wash down any particles of the sample adhering to the neck of the flask. Heat cautiously over the naked flame of a Bunsen burner until frothing has ceased, then increase the temperature until vigorous boiling commences, and maintain at this temperature until the solution becomes colorless, and for one hour thereafter. The flask should be shaken occasionally during digestion, which will require a total of about 2.5 hrs. Next, remove the flask from the flame and add in small portions sufficient potassium permanganate to produce a constant pink or green color. If the permanganate is too finely powdered flashing will occur with a resultant loss of nitrogen. About 50 mesh permanganate gives the best results. It is important that the permanganate be added immediately after removing the flask from the flame, not more than 10 sec. elapsing between the turning out of the flame and the completion of the addition of the permanganate. Allow to cool, dilute with 200 cc. of water, let stand 15 min., and transfer from the Kjeldahl flask to an Armsby copper pot containing 25 cc. of potassium sulfide solution (40 g. per liter), washing the flask with 250 cc. of water in three portions. Make strongly alkaline with saturated sodium hydroxide solution, inclining the pot so that the hydroxide will flow to the bottom without mixing, and connect at once with the distillation apparatus. Shake vigorously to insure thorough mixing. Collect the ammonia in standard sulfuric acid and complete the titration in the usual manner.

It is of the utmost importance that the delivery tube dip into the standard acid until the first rush of ammonia is over; also that the standard acid be stirred frequently in order to prevent the lighter ammonia-carrying distillate from collecting on the top, thus causing loss of ammonia.

METHOD 2. WITHOUT POTASSIUM PERMANGANATE—The manipulation in this method is identical with Method 1, except that the permanganate is omitted.

DISCUSSION

The results of nitrogen determinations on twenty-four samples are shown in Table I. The time of digestion in both methods was the same for each sample. Blanks were run on each lot of reagents and the nitrogen results were corrected for the blanks.

In every case except one (Oat Straw A) the average percentage of nitrogen is lower where permanganate was not added. The allowable difference between extremes on triplicate nitrogen determinations on feeds and feces in these laboratories is 0.05 per cent. In this series, however, all determinations are taken into consideration. Attention is directed to the wide variations between extremes where the permanganate was omitted.

It is a well-recognized fact that a loss of nitrogen occurs where flashing results from the addition of permanganate. If a loss of nitrogen occurs, as is stated by numerous authorities,[1] on addition of the permanganate even where flashing does not ensue, it is possible that the result obtained is in reality a balance figure representing compensation between a loss due to the permanganate and a gain through a more effective oxidation of the organic matter through the addition. Assuming such to be the case, the discrepancy between the conclusions drawn from determinations on this class of substances and the work reported by Frear on fertilizers may be explained. The possible presence of cyclic compounds containing nitrogen in the ring should not be overlooked.[2]

There is a wide difference of opinion among analysts as to the proper interpretation of "immediately" as used by Kjeldahl[3] in his original description of the method. It was found to be impossible with the equipment at hand to determine the rate of cooling of the sulfuric acid solution after removal of the flame. However, a series of determinations was made in which the variant was the time elapsing between cessation of boiling and the addition of permanganate.

[1] *Z. anal. Chem.*, **22**, 375; **57**, 524; **69**, 439.

[2] *J. Biol. Chem.*, **17**, 275.

[3] *Z. physiol. Chem.*, **57**, 516; **69**, 439.

Table I

	Method 1[1]					Method 2[2]					
		Nitrogen (Per cent)					Nitrogen Per cent				
Substance	No. of Determinations	Average	Individual Variations from Average		Diff. between Individual Extremes	No. of Determinations	Average	Individual Variations from Average		Diff. between Individual Extremes	Diff. between Method 1 and Method 2
			Low	High				Low	High		
Alfalfa Hay A	4	2.505	0.007	0.006	0.013	6	2.420	0.030	0.045	0.075	—0.085
Alfalfa Hay B	3	2.380	0.011	0.010	0.021	3	2.293	0.067	0.015	0.082	—0.087
Alfalfa Hay C	3	2.388	0.038	0.020	0.052	5	2.385	0.036	0.029	0.065	—0.003
Alfalfa Hay D	3	2.394	0.009	0.011	0.020	4	2.383	0.026	0.021	0.047	—0.011
Alfalfa Hay E	3	2.448	0.016	0.016	0.032	3	2.359	0.035	0.041	0.076	—0.089
Oat Straw[3] A	3	0.445	0.009	0.008	0.017	3	0.455	0.005	0.005	0.010	+0.010
Oat Straw B	3	0.528	0.019	0.009	0.028	3	0.486	0.003	0.002	0.005	—0.042
Oat Straw C	3	0.494	0.003	0.002	0.005	3	0.488	0.007	0.004	0.011	—0.006
Ref. Feed A	2	2.043	0.008	0.008	0.016	2	2.004	0.073	0.072	0.145	—0.039
Ref. Feed B	3	2.329	0.008	0.011	0.019	3	2.321	0.065	0.045	0.110	—0.008
Mixed Grain A	4	2.712	0.021	0.020	0.041	3	2.623	0.099	0.074	0.173	—0.089
Mixed Grain B	3	2.755	0.019	0.027	0.046	4	2.663	0.122	0.058	0.180	—0.092
Mixed Grain C	3	2.714	0.022	0.023	0.045	4	2.639	0.036	0.022	0.058	—0.076
Mixed Grain D	4	2.727	0.027	0.040	0.067	4	2.678	0.047	0.026	0.073	—0.049
Corn Meal A	4	1.555	0.013	0.006	0.019	3	1.503	0.076	0.043	0.119	—0.052
Linseed Meal A	3	6.354	0.013	0.015	0.028	3	6.281	0.026	0.014	0.040	—0.073
Peanut Meal A	3	6.375	0.023	0.040	0.063	3	6.256	0.010	0.006	0.016	—0.119
Comp. Feces A	3	2.799	0.025	0.028	0.053	3	2.725	0.040	0.034	0.074	—0.074
Comp. Feces B	3	3.024	0.029	0.022	0.051	3	2.966	0.029	0.034	0.063	—0.058
Comp. Feces C	3	2.563	0.022	0.007	0.027	3	2.448	0.061	0.061	0.122	—0.115
Comp. Feces D	3	2.499	0.010	0.010	0.020	3	2.474	0.006	0.008	0.014	—0.025
Comp. Feces E	3	2.413	0.011	0.010	0.021	3	2.344	0.010	0.014	0.024	—0.069
Comp. Feces F	3	2.281	0.018	0.019	0.037	3	2.219	0.024	0.021	0.045	—0.062
Comp. Feces G	3	2.163	0.017	0.018	0.035	3	2.109	0.021	0.017	0.038	—0.054

[1] Average blank on reagents 0.81 mg. N. [2] Average nitrogen per sample 25.92 mg. [3] Sample very poorly ground.

Ten seconds was found to be the minimum time required to turn off the gas, remove the flask, and add the permanganate.

Table II

	$KMnO_4$ Added		
Substance	10 Sec. Nitrogen[1] Per cent	2 Min. Nitrogen Per cent	No $KMnO_4$ Nitrogen Per cent
Alfalfa Hay	2.422	2.379	2.311
Alfalfa Hay	2.458	2.448	2.397
Mixed Grain	2.755	2.732	2.643
Feces	2.499	2.475	2.439

[1] All nitrogen results are the average of three determinations.

Here again the results obtained are decidedly in favor of the permanganate. No tendency to flash was apparent after 2 min. Hence it would seem that if flashing is dependent on temperature the critical point must be between 10 sec. and 2 min. after cessation of boiling.

CONCLUSIONS

1—The claim that the addition of permanganate in the Kjeldahl method causes loss of nitrogen is not substantiated by the results obtained on feeds and feces.

2—Nitrogen determinations made without the addition of permanganate on feeding stuffs and feces are less concordant, and are uniformly lower than those in which permanganate is used.

NOTE ON THE CATALYSIS OF PERMANGANATE TITRATIONS

By Paul H. Segnitz

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Received May 29, 1920

In titrations where permanganate solutions are used as oxidizing agents against such reducers as hydrogen peroxide in acid solution, or sodium oxalate (Sörensen's reagent), directions usually provide for the very slow addition of the first few drops of the permanganate solution, as otherwise the reaction will be greatly retarded and in extreme cases there may be the formation of the difficultly soluble manganese dioxide. The time taken by this careful procedure is sometimes sufficiently great to cause serious delay. In the case of blank tests with hydrogen peroxide, and in the standardization with sodium oxalate where heating to 70° C., as generally recommended, is inconvenient, another method of increasing the reaction velocity is highly desirable.

The permanganate reaction in the cases mentioned has been studied in detail[1] and its sluggishness has been explained as being due to the fact that this is a case of autocatalysis, that is, the reaction, of low velocity at the start, is cumulatively catalyzed by one of the reaction products, $MnSO_4$. To prove the practical value of this fact in routine titration work two series of experiments were run, using $MnSO_4$ in dilute solution as catalyst. To one gram of $MnSO_4$ dissolved in 100 cc. distilled water, was added 0.1 per cent H_2SO_4, to prevent the discoloration of the catalyst by MnO_2 which otherwise takes place.

The first series of experiments was run with the permanganate-peroxide titration according to Schaeffer[2] as in the analysis of red lead and orange mineral. The delay in the ordinary blank reaction being in this case entirely confined to the first cc. of solution used, the time required to run in this first cc. was observed as a measure of reaction velocity and effectiveness of the catalyst. Table I shows data so obtained and indicates the saving of time that may be effected by the use of the catalyst, while the end-point is unchanged.

Table I

Expt. No.	HNO_3 Soln. (Sp. Gr. 1.21) Cc.	H_2O_2 Soln. (1 : 3.5) Cc.	Catalyst Soln. Cc.	Time to Use 1 cc. $KMnO_4$ Sec.	Total Vol. $KMnO_4$ Cc.	Temp. at Start of Run ° C.
1	15	10	2	14	41.70	53
2	15	10	1	8	41.75	53
3	15	10	0.5	8	41.78	54.5
4	15	10	0	35 min. 18 sec.	41.82	54

A second series of experiments was run with sodium oxalate in solution acidified with H_2SO_4. This reaction has been extensively studied,[3] and it has been shown that the rate varies with the varying reagent

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[1] Harcourt to Esson, *Phil. Trans.*, **156** (1866), 20; Harcourt, *J. Chem. Soc.*, **20** (1867), 460; Schilow, *Ber.*, **36** (1903), 2735; *Z. physik. Chem.*, **42** (1903), 661; Skrabal, *Z. anal. Chem.*, **42** (1903), 329; *Z. anorg. Chem.*, **42** (1904), 60; *Z. Elektrochem.*, **11** (1905), 653.

[2] This Journal, **8** (1916), 237.

[3] Harcourt, Schilow, Skrabal, *Loc. cit.*

Table II

Expt. No.	1	2	3	4
Wt. sodium oxalate, g.	0.2000	0.2000	0.2000	0.2000
Temp. at start of run	70°	22.5°	22.5°	22.5°
Vol. catalyst soln. used, cc.	0	0	5	10
Vol. $KMnO_4$ required, cc.	33.90	33.87	33.85	33.85
Time for 1 cc.	1 min. (—)	4 min. 11 sec.	1 min.	45 sec.
Time for entire titration	Moderately rapid	1 hr. (approx.)	9 min. 30 sec.	6 min.

masses during the course of the process. In this run the permanganate was added several drops at a time with constant agitation, as rapidly as the solution cleared, each addition being made while the solution was still faintly pink. The acidity was about 1 per cent H_2SO_4, but as it was not controlled as carefully as in the preceding case, and as this, as well as the mass of $KMnO_4$, affects the rate, the time for these runs was taken for the entire titration, and was not so accurately observed as in the preceding experiment. Nevertheless, Table II shows an effect similar to that already shown.

CONCLUSION

These experiments indicate that the addition of $MnSO_4$ solution to permanganate titrations is a practicable method of increasing reaction velocity, in that the time of the peroxide-permanganate titration can by this means be reduced from about 35 min. to 8 sec., and that of the cold oxalate-permanganate titration from over an hour to 6 min. for the entire titration. The use of the catalyst does not affect the accuracy of the end-point.

LABORATORY AND PLANT

THE PRESERVATION OF BAGASSE IN SUGAR-CANE MILL CONTROL[1]

By Guilford L. Spencer

Cuban-American Sugar Co., 129 Front St., New York, N. Y.

A review in the March 1920 issue of the *International Sugar Journal*, page 169, calls attention to the deterioration of bagasse composite samples as regards sucrose content. In this review two chemists report decomposition even in the presence of formaldehyde or chloroform, and a third chemist's experiments show no loss of sugar after 8 hrs. storage in a stoppered bottle without antiseptic.

The writer began the use of formaldehyde as a preservative of samples in the laboratory, and of juices and meladura in the factory in the season of 1903 to 1904 in Cuba. He abandoned its use except for very short storage periods for juices (1 hr.) and bagasse (6 hrs.), on account of inversion of sucrose by the plant acids and not on account of ferments. At that time, however, experiments indicated formaldehyde to be a fairly safe preservative for bagasse for short periods. Formaldehyde is extensively used, and is without a rival in the protection of juice and meladura, during forced stoppages of the factory, though loss by inversion is known to occur. It is possible that the present very heavy milling with long trains of mills and with large use of maceration water, as compared with the conditions of a few years ago, may be in part causes of the unsatisfactory results now obtained with formaldehyde.

In accounting for irregularities in bagasse tests, the writer recently found these to be due to the inefficiency of formaldehyde in protecting the samples. There was usually no evidence of fermentation, and it is probable that the loss of sucrose was due to inversion. This led to renewed experimentation with strong ammonia, as proposed and practiced in Egypt by the late Henri Pellet.

The bagasse is collected in covered cans in a very strong atmosphere of ammonia. Cotton, saturated with strong ammonium hydroxide, is placed in perforated tin boxes at the top and bottom of the bagasse container. The ammonia thoroughly permeates the bagasse, saturates the acids, and imparts a characteristic yellow color to the sample. The analysis of the bagasse is conducted as usual, except that no sodium carbonate need be added in the digestion, and the water extract must be acidulated with acetic acid prior to clarification with subacetate of lead.

In comparative tests of finely comminuted bagasse, the samples were analyzed immediately, after storage with formaldehyde, and after storage with ammonia, for periods of 3 and 6 hrs. The formaldehyde sample showed a loss after 3 hrs. and a considerable loss after 6 hrs. The ammonia sample lost 0.1 per cent sucrose in 6 hrs. The sample originally contained 3 per cent of sucrose. Therefore, formaldehyde is not apparently a safe preservative for bagasse.

It is the writer's expectation to have made many comparative tests, using ammonia in preserving bagasse samples, with a view to arriving at more definite information. A combination of ammonia for saturating the plant acids and an antiseptic for preventing fermentation is desirable. Preliminary experiments indicate that bagasse may be preserved for periods of several hours in an atmosphere of ammonia and chloroform. This is also effective in preserving filter press-cakes.

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[1] Presented before the Section of Sugar Chemistry at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

THE SPECIFIC HEAT OF PETROLEUM AT DIFFERENT TEMPERATURES[1]

By F. W. Bushong and L. L. Knight

Research Laboratory, Gulf Refining Co., Port Arthur, Texas

The work herein described was undertaken to determine the rate of increase in the specific heat of petroleum with rise in temperature. The apparatus employed was the Parr standard calorimeter, which gave results of sufficient accuracy for technical work. The bomb was charged with benzoic acid, as recommended for the standardization of the instrument, and the oil or other liquid under examination was employed as the calorimeter fluid.

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[1] Presented before the Division of Industrial and Engineering Chemistry at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

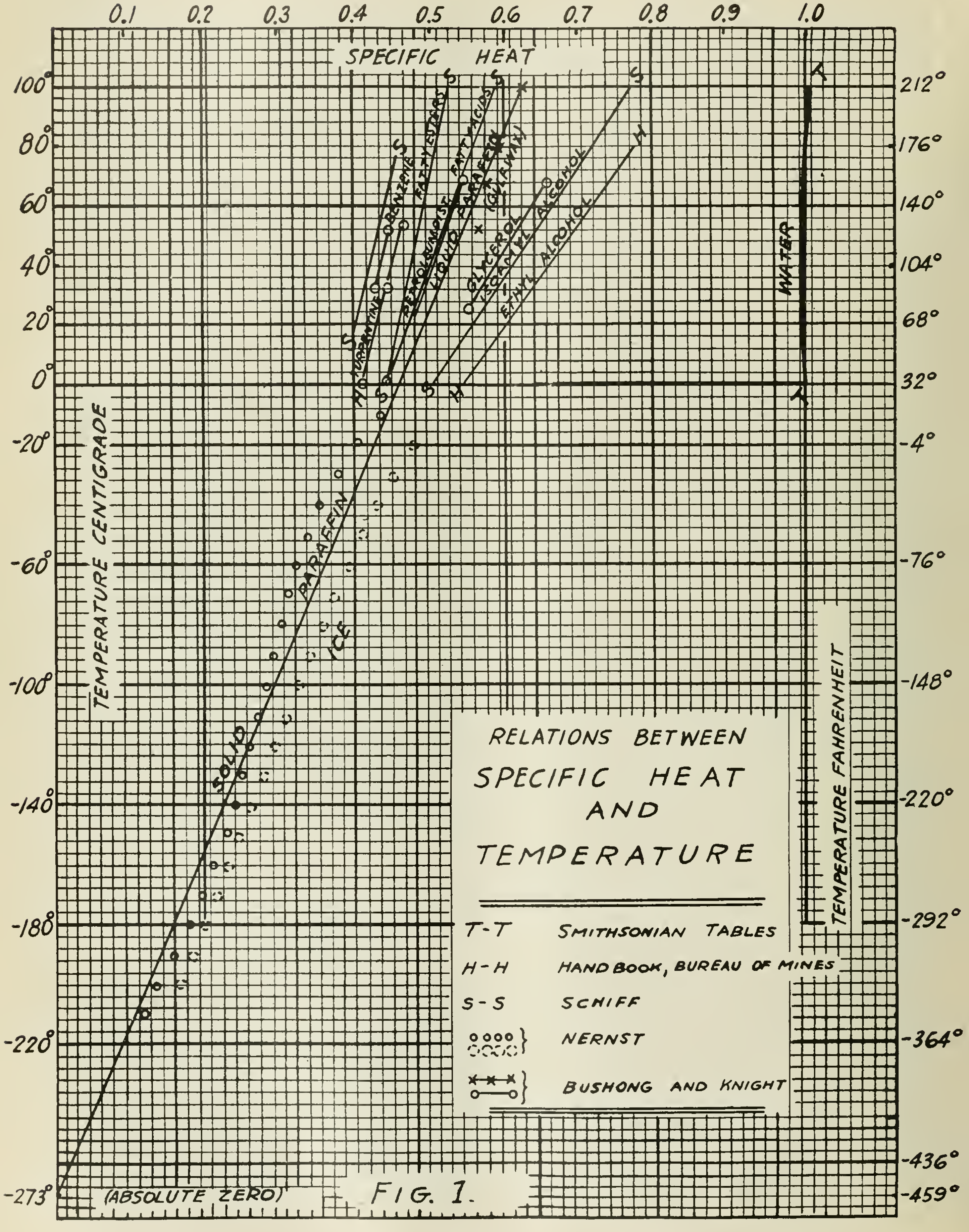
SPECIFIC HEAT
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
TEMPERATURE CENTIGRADE
100°
80°
60°
40°
20°
0°
-20°
-60°
-100°
-140°
-180°
-220°
-273°
(ABSOLUTE ZERO)
TEMPERATURE FAHRENHEIT
212°
176°
140°
104°
68°
32°
-4°
-76°
-148°
-220°
-292°
-364°
-436°
-459°
TURPENTINE
BENZINE
FATTY ESTERS
PETROLEUM OILS
FATTY ACIDS
LIQUID PARAFFIN
PARAFFIN (GULF WAX)
GLYCEROL
AMYL ALCOHOL
ETHYL ALCOHOL
WATER
PARAFFIN
ICE
SOLID
RELATIONS BETWEEN SPECIFIC HEAT AND TEMPERATURE
T-T SMITHSONIAN TABLES
H-H HANDBOOK, BUREAU OF MINES
S-S SCHIFF
NERNST
BUSHONG AND KNIGHT

FIG. 1.

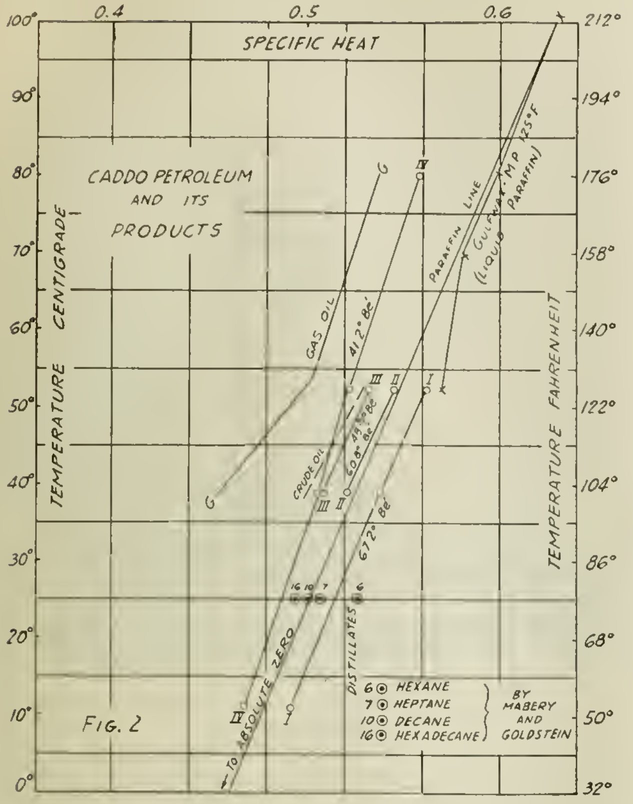

FIG. 2

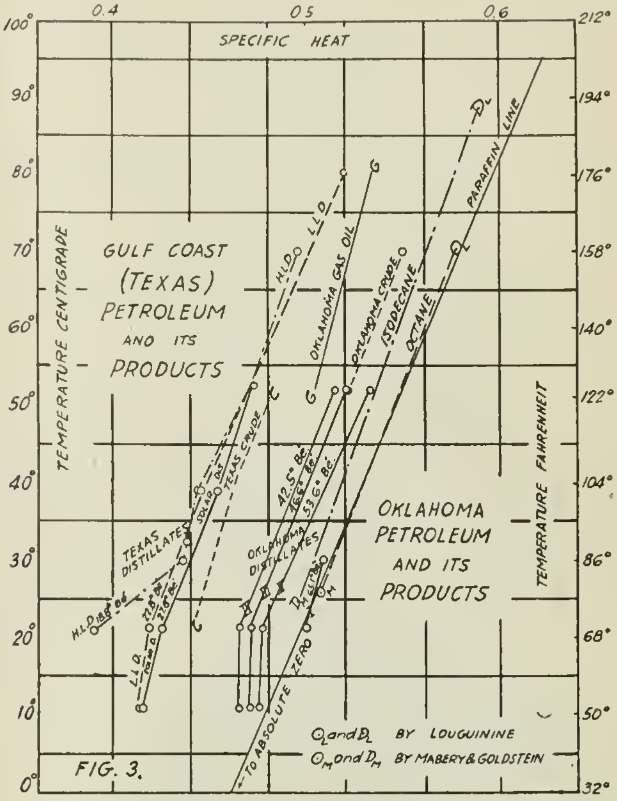

FIG. 3.

In determinations or standardizations made with the calorimeter fluid one or two degrees below room temperature, the calculations were made in accordance with the directions furnished with the calorimeter. At other temperatures it was necessary to take into account the rates of radiation established before the ignition of the charge and after the maximum rise. These rates were laid off on coördinate paper against the observed rise, and the points representing them were joined by a straight line upon which one-minute intervals were laid off. The sum of the temperature values apportioned to the minute intervals was applied as a radiation correction to the observed rise. The specific heat was calculated as follows:

The number of calories absorbed by the apparatus was found by multiplying the water equivalent (123.3 g.) by the corrected rise. This was deducted from the heat generated in the bomb (4869 cal. in case of the usual charge), giving the number of calories absorbed by the oil. By dividing this number by the corrected rise and by the weight of the oil (in grams), the specific heat was obtained.

For the standardization of the method, water was employed up to 105° F. At higher temperatures the heat losses due to evaporation of water were so great as to introduce considerable errors. Similarly in making determinations below room temperature, errors due to condensation were introduced. High viscosity is an unavoidable source of error which cannot be neglected in the consideration of the results.

Schiff has shown that the effect of temperature upon specific heat is the same for organic liquids of the same chemical nature, specific heat being a linear function of temperature. Curves representing the specific heat of the different members of a given class are, therefore, parallel straight lines.

The results obtained by the method just described, together with those taken from chemical literature, are presented in the form of curves.

They show that the specific heat of the petroleum hydrocarbons, including paraffin, is proportional to,

Data for Fig. 1

Temperature ° C.	Water Sp. Ht.	Liquid Paraffin Sp. Ht.	Ethyl alcohol	Sp. Ht.
110	1.0116	....	0° C.	0.5475
100	1.0065	0.6307	80° C.	0.7694
80	1.0024	0.5974		
68	....	0.5798	Isoamyl alcohol	
65	1.0000	....	0° C.	0.5012
52	....	0.5700	100° C.	0.7712
30	0.9974	....		
15	1.0000	....	Glycerol	
0	1.0087	....	26.5° C.	0.5523
			68.0° C.	0.6541
	Ice	Solid Paraffin	Petroleum distillates—Mean[1]	
0	....	0.47	21.1° C.	0.4703
—10	0.535	0.43	68.0° C.	0.5420
—20	0.478	0.40		
—30	0.450	0.375	Fatty acids	
—40	0.428	0.35	0° C.	0.4440
—50	0.409	0.34	100° C.	0.5858
—60	0.392	0.32		
—70	0.374	0.31	Fatty esters	
—80	0.358	0.30	0° C.	0.4416
—90	0.341	0.29	100° C.	0.5296
—100	0.325	0.28		
—110	0.307	0.27	Turpentine	
—120	0.293	0.26	0° C.	0.4110
—130	0.277	0.25	33° C.	0.4414
—140	0.262	0.24	53° C.	0.4639
—150	0.245	0.23		
—160	0.230	0.21	Benzene	
—170	0.215	0.20	32.2° C	0.4247
—180	0.199	0.18	52.2° C.	0.4449
—190	0.183	0.16	Benzene and homologs	
—200	0.168	0.14	20° C.	0.4042
—210	....	0.12	80° C.	0.4668

[1] This is the mean derived from about 200 determinations on distillates obtained from the various oils examined by the authors. Rate of increase 0.00153 per degree C.

or a function of, the absolute temperature.[1] Abnormal deviations probably indicate change in state of aggregation.

DATA FOR FIG. 2

CADDO PETROLEUM AND ITS PRODUCTS

		Gravity ° Bé.	52° F.	102° F.	126° F.	155° F.	176° F.	212° F.
c—c	Crude oil	40.6	....	0.5003	0.5283	....	....	....
o—o	Distillates:							
	I....	67.2	0.4933	0.5382	0.5620	....	....	....
	II....	60.8	....	0.5217	0.5462	....	....	....
	III....	48.9	....	0.5083	0.5326	....	....	....
	IV....	41.2	0.4688	0.5074	0.5228	....	0.5591	....
x — x	Paraffin— m. p. 125° F.:		....	....	0.5700	0.5798	0.5974	0.6307
G—G	Gas oil...	27.1	....	0.4554	0.5006	....	0.5432	....

HYDROCARBONS AT 25° C.

O_6 Hexane	0.5272
O_7 Heptane	0.5074
O_{10} Decane	0.5021
O_{16} Hexadecane	0.4957

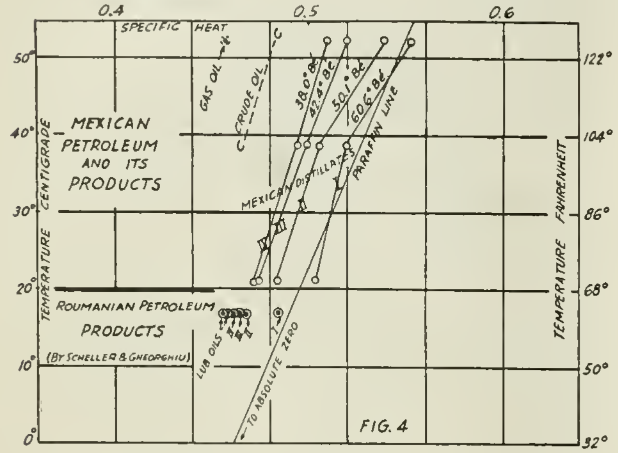

FIG. 4

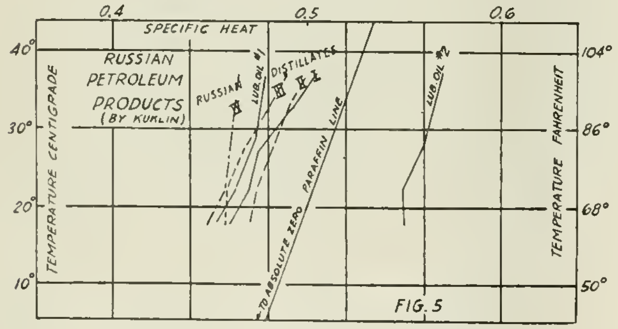

FIG. 5

DATA FOR FIG 3

OKLAHOMA PETROLEUM AND ITS PRODUCTS

		Gravity ° Bé.	52° F.	70° F.	89° F.	126° F.	155° F.	176° F.
c—c	Crude oil	36.1	....	....	....	0.5192	....	....
o—o	Distillates:							
	I....	65.1	....	0.4982	0.5094	....	....	....
	II....	53.6	0.4751	0.4772	....	0.5328	....	....
	III....	47.6	0.4706	0.4704	....	0.5210	0.5503	....
	IV....	42.5	0.4655	0.4658	....	0.5159	....	....
G—G	Gas oil...	27.6	....	....	....	0.5038	....	0.5338

GULF COAST (TEXAS) PETROLEUM AND ITS PRODUCTS

		Gravity ° Bé.	52° F.	70° F.	86° F.	91° F.
c—c	Crude oil.......	20.8	....	0.4406	....	....
o—o	Distillates:					
	Solar........	27.8	0.4150	0.4253	....	....
	L. L. D......	22.8	0.4135	0.4187	....	....
	H. L. D......	18.8	....	0.3905	0.4358	0.4385
			102° F.	126° F.	155° F.	176° F.
c—c	Crude oil............		0.4624	0.4823	....	....
o—o	Distillates:					
	Solar...............		0.4532	0.4729	....	....
	L. L. D............		0.4465	0.4727	....	0.5207
	H. L. D............		0.4443	0.4724	0.4956	....

HYDROCARBONS

		25° C.	71.8° C.	88.3° C.
O_M	Octane................	0.5052	....	....
O_L	Octane................	....	0.5782	....
D_M	Isodecane.............	0.4951	....	....
D_L	Isodecane.............	....	....	0.5899

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[1] This appears to be a special case in which specific heat and entropy are proportional, $a \frac{C_p}{T} = \frac{Q}{T}$, and perhaps equal.

DATA FOR FIG. 4

MEXICAN PETROLEUM AND ITS PRODUCTS

		Gravity ° Bé.	70° F.	102° F.	126° F.
c—c	Crude oil..........	21.0	....	0.4667	0.4813
o—o	Distillates:				
	I.............	60.6	0.5021	0.5197	0.5509
	II.............	50.1	0.4836	0.5055	0.5384
	III.............	42.4	0.4736	0.4983	0.5193
	IV.............	38.0	0.4715	0.4933	0.5103
G	Gas oil...........	11.9	....	....	0.4573

ROUMANIAN PETROLEUM PRODUCTS

Distillates:	16° C.
I	0.4840
II	0.4679
III	0.4652
IV	0.4619
Lubricating oil, 1	0.4579
Lubricating oil, 2	0.4567

DATA FOR FIG 5

RUSSIAN PETROLEUM PRODUCTS

Distillates:	17.5° C.	22.5° C.	27.5° C.	32.5° C.	37.5° C.
I..............	0.459	0.469	0.475	0.490	0.505
II..............	0.469	0.474	0.481	0.489	0.501
III..............	0.457	0.459	0.469	0.480	0.488
IV..............	0.449	0.459	0.460	0.463	0.465
Lubricating oil, 1......	0.452	0.463	0.471	0.475	0.479
Lubricating oil, 2......	0.550	0.550	0.559	0.566	0.571

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A NEW ILLUMINATOR FOR MICROSCOPES. III[1]

By Alexander Silverman

SCHOOL OF CHEMISTRY, UNIVERSITY OF PITTSBURGH, PITTSBURGH, PA.

Since the publication of the first and second papers,[2] the following new points have been developed in connection with the construction and use of the new illuminator[3] for microscopes.

CHANGES IN CONSTRUCTION

THE LAMP—This is made as previously described, except that the lead-in wires are held together by a fused glass bead so as to prevent their being bent at glass terminals of the lamp. Through this improvement breakage has been eliminated.

THE RHEOSTAT—For the upright cylindrical rheostat described in the second paper a flat, rectangular one (Fig. 1) has been substituted, which is controlled by a push-button switch delivering 0.9 ampere and 13.5 volts for visual work and a spring-contact switch, operable independently of the push button, and delivering 1.06 amperes and 18 volts for photographic work.

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[1] Read before the New York Section of the American Chemical Society, June 11, 1920.

[2] THIS JOURNAL, **9** (1917), 971; **10** (1918), 1013.

[3] U. S. Patents 1,311,185, 1,311,186, 1,257,287; Brit. Patent 125,187; Canadian Patent 185,283; Italian Patent 48,485; French Patent 489,304. Other foreign patents pending.

STAGE ADAPTER—An adjustable illuminator support which is clamped to the stage has been devised for bringing the light closer to the object than would be possible were the illuminator clamped directly to the objective for low power work. This adapter also makes the illuminator available for use on binocular microscopes of the double-objective type (Fig. 2).

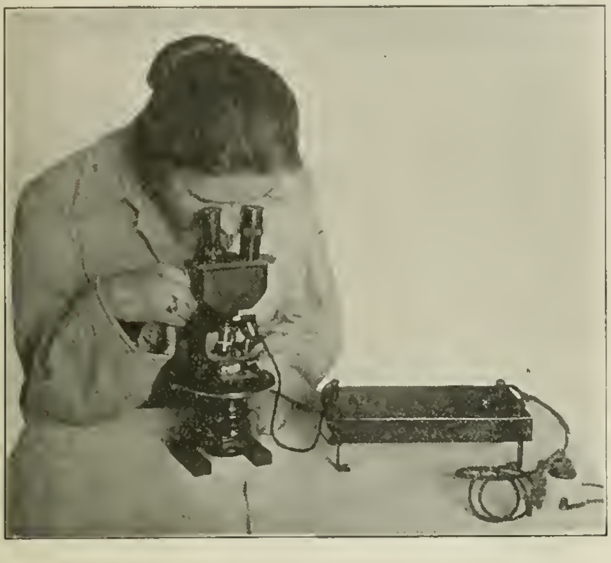


FIG. 1

SUGGESTED APPLICATIONS OF THE INSTRUMENT

DEFINITION IN PHOTOGRAPHING—A number of suggestions have been received from users of the device. Dr. R. Thiessen, of the United States Bureau of Mines, states that when the light was turned off before removing the cover from the plate holder images were out of focus, due to contraction of the brass in the objective. By allowing the lamp to burn during this operation the trouble was eliminated and clear images were obtained on the plates.

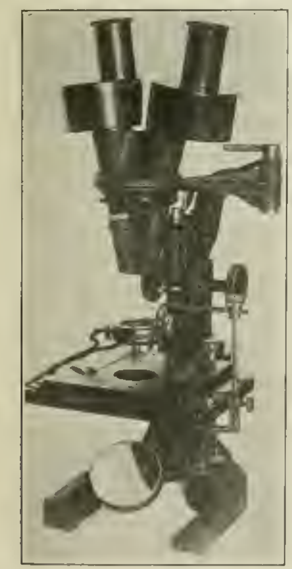


FIG. 2

Dr. Thiessen also states that the illuminator proved satisfactory for the examination of clay structure in graphite crucibles after all other methods of illumination had failed. Fig. 3 shows a section of a crucible from which the graphite was burned after polishing and before photographing. The magnification is 200×. A combination of Zeiss 16 mm. apochromatic objective with 8× compensating eye-piece was employed.

Mr. S. C. Akehurst, F. R. M. S., has used a Davies' shutter (tube containing iris-diaphragm) between the objective and the tube of the microscope. A large aperture was used for focusing and a small one, with an exposure of from 1 to 4 min., for photographing. The use of the Davies' shutter insures greater definition.

ABSORPTION SCREENS—Mr. Akehurst has also experimented on the use of color screens and has found it possible to place small, thin disks of colored gelatin in the objective or over the eye-piece with good results and with no effect on the resolving power of the lenses. The writer is having lamps made in various colors for experimental purposes.

COMPARISON WITH VERTICAL-ILLUMINATOR IMAGES—Mr. J. J. Wilson, of the National Tube Company, has prepared contact plates from negatives of steel samples made with the new illuminator. Prints from the positive plates have the same order of dark and light effects as those from negatives obtained with the vertical illuminator. Depressions and relief images show better under the new light, and cleavage lines between crystals, which are not visible under vertical light, are brought out by the new method.

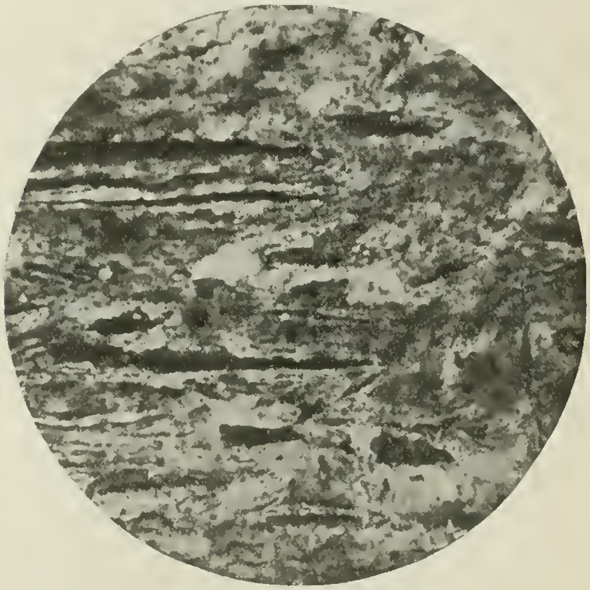


FIG. 3

SUB-STAGE ILLUMINATION—Mr. E. F. Lowry, of the University of Pittsburgh, reports that he inverted the stage adapter, had the light of the lamp fall on the concave mirror placed parallel to the stage, and photographed thin sections of cork successfully by transmitted light.

MINERAL SECTIONS—A number of mineralogists have called attention to uses of the new lamp in the study of mineral sections. Transparent portions may be viewed by transmitted light but the new illuminator "proves particularly serviceable in the examination of opaque or metallic minerals present in ordinary thin sections." "In the examination of opaque ores in the form of polished slabs, as in metallography, the new illuminator is of value, but cannot replace the vertical illuminator, as methods of identification of ores, such as sulfides, are based on the text of Murdock ('The Determination of Opaque Minerals') in which colors listed depend on vertical light."

A new text is desirable which will list mineral colors seen under the new illuminator.

The writer desires to thank the above-mentioned gentlemen and many others who have been kind enough to make suggestions and send photomicrographs.

A NEW CONDUCTIVITY CELL

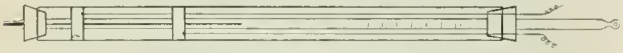
By Frank E. Rice

Department of Chemistry, Cornell University, Ithaca, N. Y.

Received August 6, 1920

The measurement of electrical conductivity of solutions is being more and more employed in manufacturing operations for the control of processes. In such instances a high degree of accuracy is unnecessary, since comparative results are more important than absolute. The one thing necessary is an apparatus sturdy, simple, and easy of adjustment, so that a trained physicist need not be employed for its operation.

At the present time there may be obtained on the market all the electrical parts necessary for the installation of a Wheatstone bridge of such form that it may be easily manipulated without any adjustment or attention. As a source of current, a 60-cycle line may be drawn upon; alternating current galvanometers were found sufficiently sensitive for practical work.



A NEW CONDUCTIVITY CELL

As an adjunct to such equipment the conductivity cell here described may be prepared by the amateur glass blower in a short time. It will be found strong and easily cleaned. In the accompanying drawing the idea is diagrammatically illustrated, though the dimensions and particular arrangement of parts may be varied at will.

A glass tube about the size of an ordinary buret is used for the case. Platinum wires are blown through the sides of this tube some distance apart. Platinum bands made to fit snugly around the tube are soldered closely to the outside ends of the wires. The inside ends are long enough to reach to one end and outside the tube; the inside portion of one wire is covered with small glass tubing for the purpose of insulation.

Since the temperature of the solution in which measurement is made is usually important, a thermometer passes through the tube. This thermometer should be of considerable accuracy and one graduated in 0.2° C. is suggested. This should be planned, however, to accord with the accuracy desired, and will depend also upon the thermal coefficient of the solutions in which measurements are made. The ends of the tube are finally closed with rubber stoppers.

The distance between the band electrodes and their size should be gaged by the conductivity of the liquid in which the cell is to be used. That an idea may be obtained of the constant to be expected, the following result is reported on one cell which has been used. (The electrodes are platinized.)

Circumference of band	43 mm.
Width of band	6 mm.
Distance apart (inside to inside)	41 mm.
Resistance recorded of 0.01 N KCl at 18° C	261 ohms
Constant of cell	0.321

The above measurement was made by holding the cell upright in the solution, using a 500 cc. wide-mouthed bottle as the container. Since the paths of current flow are wholly outside this apparatus, it is essential that the vessel containing the solution be always of the same dimensions in order to insure comparative results. Furthermore, the position of the cell in the vessel should always be the same. These precautions apply, of course, unless the container is of great size.

ADDRESSES AND CONTRIBUTED ARTICLES

AMERICAN PROGRESS IN THE BACTERIOLOGICAL SUGARS[1]

By Edmund H. Eitel

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The history of the carbohydrates covers a brief period of time, during the last ten years of which a large part of the progress in methods of preparation is to be found in American chemical literature, and practically all of the progress in commercial methods has been due to American ingenuity.

The prime investigator in the chemistry of the rare sugars was Emil Fischer, who began his well-known researches in 1883. The first to make a reasonably direct use of the sugars in bacteriology was Escherich, who thirty-four years ago wrote one of the great bacteriological classics, "The Intestinal Bacteria of Nurslings." By 1902, the possibilities of fermentation reactions with the carbohydrates were recognized by many bacteriologists, and at this time Martini and Lentz introduced the use of mannitol to differentiate the Shiga from the Flexner bacillus. Later intensive studies of bacillary dysentery in America by Park and Dunham, Hiss and Russell, and by others, differentiated by means of sugar fermentation other strains in the dysentery group, and thus the carbohydrates were established as a necessary aid in bacteriology.

Germany was the only commercial source of supply for the rare sugars before the war. During the war the stocks of sugars on hand were in most cases soon exhausted, and the U. S. Army Medical School, and other investigators using the sugars in colon-typhoid and other important differentiations, found their work critically handicapped at the moment it became most vital to the nation.

Owing largely, however, to the researches of such men as Hudson and his co-workers of the Bureau of Chemistry of the U. S. Department of Agriculture, and Levene and his associates in the Rockefeller Institute, methods were developed for preparing the necessary rare sugars in this country. The Carbohydrate Laboratory of the Bureau of Chemistry had been engaged since 1909 in investigating the rare sugars and their derivatives, and this work was continued during the war, and considerable quantities of various sugars were prepared They were similarly produced at the Rockefeller Institute, where of special interest were the researches of Levene and Jacobs, who succeeded in synthesizing allose and altrose, thus filling in the last gap of the aldohexose series.[1] It is a significant fact that the methods of preparation given in the standard German treatises (Tollens, von Lippman, etc.) are now more or less antiquated, due to the progress made by the Bureau of Chemistry, the Bureau of Standards, Rockefeller Institute, and American industrial concerns. To translate this statement into its practical significance, it may be observed here that the prices at which the rare sugars, with the exception of levulose, are now available in America, reflect this progress, being in several instances below the pre-war figures, in spite of the far higher price levels of the present day.

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[1] Presented before the Sugar Section at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

The work of the Bureau of Chemistry included the production of twenty-one carbohydrates and no less than 150 derivatives. Through the researches of Dr. F. B. LaForge, two new sugars, the only heptoses thus far found in nature, were discovered, manno-keto-heptose in the avocado, and sedoheptose in the stonecrop.[2] Another work of note was the contribution made by Dr. Hudson and his co-workers toward solving the relation between structure and optical activity, accomplished mostly through the study and preparation of the various acetyl derivatives.[3] Mention should also be made of the fact that a more general use of glacial acetic acid, almost essential in many of the sugar methods, was developed in the Bureau of Chemistry.

During the war an appeal was made by the Medical Department of the U. S. Army, not only to the public institutions above mentioned, but to individuals, to produce certain sugars urgently required and not then to be had. Largely as a patriotic measure, a few individuals, first in private laboratories, undertook to prepare certain sugars needed in quantity, and from this beginning their manufacture was undertaken industrially. It should be noted that the industrial stage represents a distinct advance, since the production of gram lots in the laboratory is child's play compared to manufacture in commercial quantities. The history of the development of cane- and beet-sugar manufacture illustrates the significance of the foregoing observation, which applies not to one but to a score of sugars obtained from as many different sources.

In spite of the research and development expense required to put large-scale manufacture on a satisfactory basis, and in spite of the limited demand for the sugars to date, not all the manufacturers who have attempted their commercial production have abandoned it, but continue in the hope that an increased demand for some purpose will soon be forthcoming. Because of the importance of the sugars to public health and in order to help place the national health beyond the control of foreign countries, the rare sugars were added to the Longworth Dye Bill.

The rare sugars now manufactured commercially in this country are the following:

l-Arabinose, dulcitol, *d*-galactose, *d*-glucose, glycogen, inositol, inulin, invert sugar, lactose, *d*-levulose from invert sugar, *d*-levulose from inulin, levulose sirupy, maltose, *d*-mannitol, *d*-mannose, melezitose, raffinose, rhamnose, sorbitol, sucrose, trehalose, and *l*-xylose.

Sugars are being produced in this country in a higher degree of purity than were those formerly imported from abroad. The latest model of Dr. Frederick Bates' improved sensibility polariscope has contributed to the higher standard of analysis, as has also the increasing knowledge of American bacteriologists of the minute impurities which may give misleading results. But above all, the stricter standard is due to a policy of putting purity above manufacturer's costs and profits, because of the requirements and importance of the science of bacteriology.

An instance of the minute quantity of impurity detectable bacteriologically is the case of lactose, which is one of the sugars most rarely obtained in a degree of purity suitable for bacteriology. This is used in important differentiations for *B. typhosus*, which will not ferment lactose; but if minute quantities of glucose or galactose are present, an apparent fermentation of lactose occurs. To illustrate what seemingly insignificant amounts of impurities will give misleading results in bacteriology, the culture media are ordinarily prepared with one per cent of lactose. Yet Dr. Arthur I. Kendall, the bacteriologist to whom the author is indebted for many of the latest facts in bacteriology incorporated in this paper, has made experiments in his laboratory with glucose present in lactose to the extent of only 0.05 per cent, and the bacteria have indicated the impurity visibly. The same thing is notably true of impurities in sucrose. It is no mean achievement of American chemists to have manufactured lactose and sucrose and the other sugars of the required purity, and yet there is no alternative if accurate results are to be obtained. The rare sugars which are being tried in countless reactions are worse than useless if not absolutely pure, and one of the obstacles to progress in bacteriological research has been the lack, until recently, of uniformly pure sugars, making it possible for one experimenter to check or duplicate another's work or to repeat his own experiments with uniform results.

USES OF THE SUGARS

Before describing the uses of the sugars in bacteriology, where their chief importance now lies, it may be of interest first to indicate their general value and their possibilities in other directions.

Dr. E. Frankland Armstrong says in his recent monograph,[1] "Probably in no other branch of chemistry......is so great an opportunity afforded for the study in detail of the influence of structure on the properties of the molecule. Much has already been done in this direction, but we are only upon the threshold of the inquiry." Raffinose is used in physicochemical measurement of the degree of hydration of ions. Other sugars are used as control reagents in carbohydrate analysis. Mannitol is used in borax determinations in fertilizer analysis. Levulose is valuable for diagnosing certain pathological conditions of the brain. Mannitol has been used in the preparation of the detonator, hexanitromannitol. Glucose, lactose, and maltose are important in experimental nutrition, and have, of course, graduated out of the class of rare sugars and found broad uses in technical grades. Glucose has especial importance in typhoid diet. This sugar, because it is the form in which the carbohydrate is carried in the blood stream, is being injected intravenously in cases of shock, particularly following operations and in cases of exhaustion in pneumonia. Dr. R. T. Woodyatt and Dr. W. D. Sansum, of Chicago, and Dr. Russell M. Wilder, of the Mayo Clinic, have studied and developed this use for glucose as described in the literature.[2]

As illustrative of the wide use of the sugars even in the human body, the following will be suggestive of future fields for the use of the carbohydrates. Practically all of the carbohydrates taken into the body, with the exception of levulose and galactose, must be converted to glucose before being assimilated. Glucose is found in normal blood to the extent of 0.08 to 0.14 per cent. So far as is known, the digestive tract is able to assimilate all of the carbohydrates which are found in nature, with the exception of inulin. Dr. H. B. Lewis, of the University of Illinois, declares inulin is not assimilated. This is due to the fact that there are no specific enzymes in the intestine which convert this carbohydrate to a form which can be utilized by the body. The enzyme maltase converts maltose into two molecules of glucose; lactase converts lactose into glucose and galactose; sucrase converts sucrose into glucose and levulose. The normal individual consumes between 500 and 600 g. of carbohydrate daily. The carbohydrate is the most important food because it is the easiest form of food for the body to oxidize; in other words, the body can get more energy from carbohydrate for the proportion of energy expended than from the proteins or fats. In fact, as is often said, "the fats burn in the fire of the carbohydrates," or, in other words, carbohydrate must be present in proper proportion to secure the proper utilization of fat.

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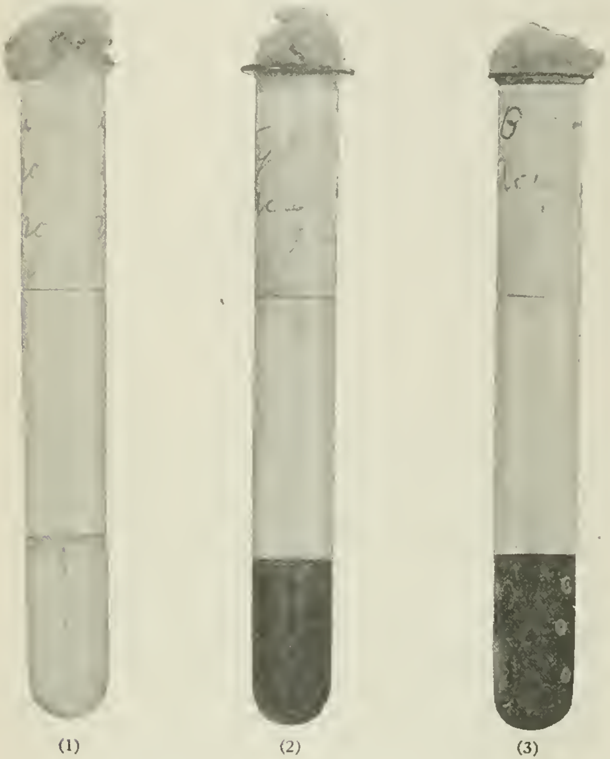
[1] *Ber.*, **43** (1910), 3141.

[2] *J. Biol. Chem.*, **28** (1917), 511; LaForge and Hudson, *Ibid.*, **30** (1917), 61.

[3] Hudson, Nichols Medal Address, THIS JOURNAL, **8** (1916), 379.

[1] "The Simple Carbohydrates and the Glucosides," Longmans, Green & Co., **1919**.

[2] *J. Am. Med. Assoc.*, Dec. 11, 1915, 2067; *Ibid.*, Oct. 27, 1917, 1410; June 23, 1917, 1885; Aug. 17, 1918, 71; Jan. 10, 1920, 75; *J. Biol. Chem.*, March 1917, 355; *Ibid.*, May 1917, 155, March 1920, 315; Ferrar, *Am. J. Obstetrics*, October 1920.



Differentiation of Bacteria with Rare Sugars

The three test tubes contain culture media with *d*-glucose (dextrose).

(1) *B. alcaligenes* leaves media unchanged.

(2) *B. typhosus* ferments glucose, producing acid which turns indicator red.

(3) *B. coli* not only ferments the sugar but produces bubbles of gas which are shown trapped in the media, stiffened with agar.

This is proved in cases of severe diabetes, where as high as from 50 to 200 g. of glucose have been excreted daily. The old method of treatment was to remove carbohydrates completely from the patient's diet. It was found that the fats were then not completely oxidized and that acetone bodies, namely, β-hydroxybutyric acid, acetoacetic acid, and acetone, appeared in larger amounts, the patient generally going into coma, and death following. The later method is not to remove carbohydrates entirely from the diet, but to cut down on all the foods in the proper proportion. This would seem to prove that a certain amount of carbohydrate is necessary for a proper utilization of fats. Levulose may be useful as a food for diabetics, as the levulose is assimilated as such into the blood stream. The body can get its energy from levulose and in this way levulose can take the place of glucose, which, in diabetics, the body is, for some reason, not able to utilize.

In certain diseases the body is unable to utilize the pentoses found in the food and they are excreted as such. This condition is called pentosuria. What would happen if the system were flooded with large amounts of pentoses is a field for interesting future research.

Glycogen, sometimes called animal starch, is extremely important, and future investigations may develop its uses. Glycogen is synthesized and found only in the animal body. It acts as a storehouse of energy for the body. In cases of starvation no glycogen is found. The glycogen content of the body is lowered by severe exercise and almost disappears in cases of severe tetanus, either natural or artificial, such as that produced by strychnine. When a starving dog, whose liver is free of glycogen, is fed on a heavy meat diet free of carbohydrate, the liver and muscles are soon found to contain a high per cent of glycogen, which fact proves that protein may be changed to carbohydrate in the body. When an animal dies, its glycogen is converted very rapidly to glucose because of an enzyme in the tissues. The quantity of glycogen found scattered throughout the animal body in some cases is as high as 15 to 18 per cent (as in the liver), and the ease with which it is converted to glucose indicates that glycogen and glucose are very closely related to the vital processes of life.

In this connection there is an interesting fact relating to the nucleus of the living cell, which is the very center of life so far as it can be determined. In the cell is a substance called nucleic acid which is found to contain a carbohydrate. The identity of this carbohydrate is an important study, and Levene and Jacobs,[1] Neuberg,[2] and Walter Jones[3] have made important investigations to identify it.

In the brain of growing infants, galactose is found in large amounts, and is always present even in the mature brain. This, perhaps, explains why nature chose lactose as the carbohydrate in milk, since the disaccharide, lactose, is composed of equal parts of glucose and galactose. This fact may partially explain why any attempt to modify human milk without the use of lactose has not been very successful. The infant seems incapable of synthesizing galactose from any other carbohydrate.

APPLICATION IN BACTERIOLOGY

While the foregoing would indicate that the possibilities of the rare sugars in the future may be great, as a matter of fact their present demand is extremely limited. They have found their chief value in differential media in bacteriology. (And even here they are used in such small quantities that the manufacturers would fall on the neck of any bacteriologist who would train his "bugs" to use more than one per cent in sugar solutions, so that the sugars might be sold in pounds instead of grams!)

Bacteria which are difficult or impossible to differentiate by morphology or by the employment of stains, are differentiated by their reactions upon the rare sugars. Bacteria either do not ferment certain carbohydrates, or else they do ferment them because of their ability to utilize these carbohydrates for their energy requirements. The acid produced in the fermentation reaction is evidenced by a color indicator, such as litmus. Many types produce gas as well. These gases are carbon dioxide and hydrogen, and the proportions in which they are produced vary more or less with the organism and with the time through which the observations are made. Brilliant work upon the gas ratios was done by Dr. Theobald Smith, of the Rockefeller Institute. The determination of the gas ratios as a means of identifying the various strains is not now considered so important as it was. In most cases, so far as we know, the cleavage of the molecule is produced by a process of hydrolysis, but, as a matter of fact, not very much is yet known about the chemical reactions.

The work with the rare sugars is done in racks of test tubes—the various sugars being arranged in rows in one direction and the various strains of bacteria being in the rows at right angles to the former. There are many refinements in methods of preparing the culture media, but since the value of these refinements is in dispute among the bacteriologists themselves, a simple statement of typical procedure will suffice. The culture media with the sugars are prepared by all bacteriologists with practically the same formula. The U. S. Army Medical School makes up its media in a typical manner as follows:

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[1] *J. Am. Chem. Soc.*, **32**, 231; *Ber.*, **42**, 1198.

[2] *Ber.*, **42**, 2806.

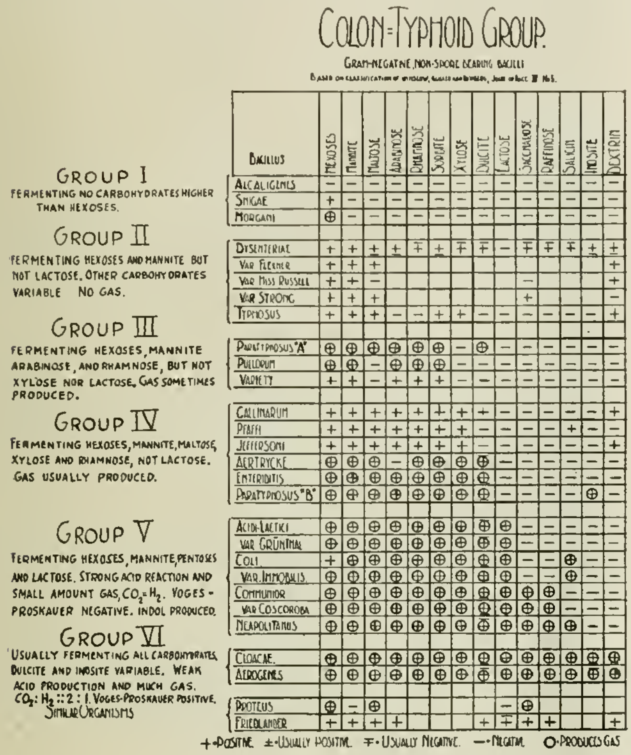
[3] "Nucleic Acids," Longmans, Green & Co., London, **1914**.

Sugar-free meat extract, beef or veal infusion

Special sugar	1.0 per cent
Peptone	1.0 per cent

End-point neutral, Andrade indicator, autoclaved for 10 min. at 10 lbs. pressure.

The accompanying chart was compiled by the U. S. Army Medical School, which is doing brilliant work under Col. Frederick F. Russell, and was loaned by Col. M. A. Reasoner, who was one of the first to appreciate the importance of the sugars to American medical research.



COLON-TYPHOID GROUP.

GRAM-NEGATIVE, NON-SPORE BEARING BACILLI

Based on classification of [illegible], Jour. of Bact. V No. 5.

	BACILLUS	HEXOSES	MANNITE	MALTOSE	ARABINOSE	RHAMNOSE	SORBITE	XYLOSE	DULCITE	LACTOSE	SACCHAROSE	RAFFINOSE	SALICIN	INOSITE	DEXTRIN
GROUP I FERMENTING NO CARBOHYDRATES HIGHER THAN HEXOSES.	ALCALIGINES	−	−	−	−	−	−	−	−	−	−	−	−	−	−
	SHIGAE	+	−	−	−	−	−	−	−	−	−	−	−	−	−
	MORGANI	⊕	−	−	−	−	−	−	−	−	−	−	−	−	−
GROUP II FERMENTING HEXOSES AND MANNITE BUT NOT LACTOSE. OTHER CARBOHYDRATES VARIABLE NO GAS.	DYSENTERIAE	+	+	±	±	∓	±	∓	∓	−	∓	∓	∓	±	±
	VAR FLEXNER	+	+	+											+
	VAR MISS RUSSELL	+	+	−							−				+
	VAR STRONG	+	+	+							+				−
	TYPHOSUS	+	+	+	−	−	+	+	−	−	−	−	−	−	+
GROUP III FERMENTING HEXOSES, MANNITE ARABINOSE, AND RHAMNOSE, BUT NOT XYLOSE NOR LACTOSE. GAS SOMETIMES PRODUCED.	PARATYPHOSUS "A"	⊕	⊕	⊕	⊕	⊕	⊕	−	⊕	−	−	−	−	−	−
	PULLORUM	⊕	⊕	−	⊕	⊕	⊕	−	−	−	−	−	−	−	−
	VARIETY	+	+	−	+	+	+	−	−	−	−	−	−	−	−
GROUP IV FERMENTING HEXOSES, MANNITE, MALTOSE, XYLOSE AND RHAMNOSE, NOT LACTOSE. GAS USUALLY PRODUCED.	GALLINARUM	+	+	+	+	+	+	+	+	−	−	−	−	−	+
	PFAFFI	+	+	+	+	+	+	+	−	−	−	−	+	−	−
	JEFFERSONI	+	+	+	+	+	+	+	−	−	−	−	−	−	+
	AERTRYCKE	⊕	⊕	⊕	−	⊕	⊕	⊕	⊕	−	−	−	−	−	−
	ENTERIDITIS	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	−	−	−	−	−	−
	PARATYPHOSUS "B"	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	−	−	−	−	⊕	−
GROUP V FERMENTING HEXOSES, MANNITE, PENTOSES AND LACTOSE. STRONG ACID REACTION AND SMALL AMOUNT GAS, $CO_2=H_2$. VOGES-PROSKAUER NEGATIVE. INDOL PRODUCED.	ACIDI-LACTICI	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	−	−	−	−	−
	VAR GRÜNTHAL	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	−	−	−	−	−
	COLI	+	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	−	−	⊕	−	−
	VAR. IMMOBILIS.	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	−	−	⊕	−	−
	COMMUNIOR	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	−	−	−
	VAR COSCOROBA	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	−	−	−
	NEAPOLITANUS	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	−	−
GROUP VI USUALLY FERMENTING ALL CARBOHYDRATES. DULCITE AND INOSITE VARIABLE. WEAK ACID PRODUCTION AND MUCH GAS. $CO_2:H_2::2:1$. VOGES-PROSKAUER POSITIVE.	CLOACAE.	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕
	AEROGENES	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕	⊕
SIMILAR ORGANISMS	PROTEUS	⊕	−	⊕						−	⊕				
	FRIEDLANDER	+	+	+	+				+	∓	+	+			+

+ = POSITIVE. ± = USUALLY POSITIVE. ∓ = USUALLY NEGATIVE. − = NEGATIVE. O = PRODUCES GAS

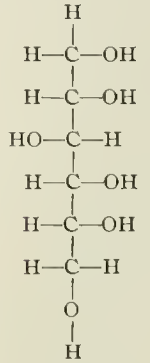
The vital importance to public health of these bacillary differentiations may be illustrated by one example from the Paratyphoid-Enteritidis group, upon the differentiation of which Dr. Edwin O. Jordan, of the University of Chicago, has done notable work.

It is important to know, especially in the case of national epidemics like that which swept Siberia in the recent war, whether human paratyphoid fever is due to infection from human sources (like typhoid fever) or from the lower animals (as is apparently true of certain "food-poisoning" outbreaks). Until Dr. Jordan made his researches there was no satisfactory method for differentiating the bacillus associated with many cases of human paratyphoid fever (*B. paratyphosus B*) from the similar bacillus found in certain epidemics of meat poisoning, or from the bacillus commonly present in the bodies of swine dying from hog cholera (*B. suipestifer*). Dr. Jordan's results[1] indicate that the differentiation may be made with xylose, arabinose, and dulcitol. While Jordan made one of his differentiations, *B. enteriditis* from *B. paratyphosus B*, by means of an agglutination test, Russell has made this differentiation by means of inositol.[2]

What are the possibilities for the specific uses of the sugars in bacteriology? The ideal would be to develop a long list of the rare sugars, or their derivatives, each of which would be fermented by one and only one strain of bacteria. No comprehensive system of this kind has yet been developed. As already pointed out, certain definite differentiations with the sugars have been made, but the work has thus far had the nature of cataloging. Much study is being devoted to the characteristic action of the hexoses and pentoses, etc., to the *d*- and *l*-configurations, and various classifications, in the hope of discovering the key to the problem. The problem cannot properly be called the bacteriologist's problem, nor indeed the chemist's problem. Whoever solves the riddle will be some rare genius who is both bacteriologist and organic chemist in one.

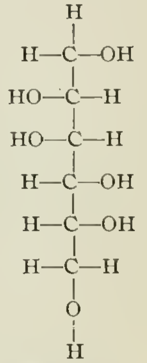
It may be interesting to give certain examples which bring us to the borderland of the known and the unknown. The sugars which are found in nature, whether *d* or *l* (and practically all are *d* sugars), are the ones which are fermented.

For instance, bacteria which will ferment *d*-glucose, *d*-levulose, *d*-mannose, and *d*-galactose, will not ferment *l*-configurations of these sugars. This brings us to theories of enzymes and enzyme action. To state another problem: Why will a very slight change in the stereoisomeric formula of a carbohydrate, or of a very small change in its terminal groups, determine its fermentability by various organisms? Why, for instance, will *B. dysenteriae Flexner* ferment *d*-mannitol and not *d*-sorbitol? According to Emil Fischer, *d*-mannitol and *d*-sorbitol have the following stereoisomeric formulas:



$$\begin{array}{c}\mathrm{H}\\ |\\ \mathrm{H{-}C{-}OH}\\ |\\ \mathrm{H{-}C{-}OH}\\ |\\ \mathrm{HO{-}C{-}H}\\ |\\ \mathrm{H{-}C{-}OH}\\ |\\ \mathrm{H{-}C{-}OH}\\ |\\ \mathrm{H{-}C{-}H}\\ |\\ \mathrm{O}\\ |\\ \mathrm{H}\end{array}$$

d-Sorbitol



$$\begin{array}{c}\mathrm{H}\\ |\\ \mathrm{H{-}C{-}OH}\\ |\\ \mathrm{HO{-}C{-}H}\\ |\\ \mathrm{HO{-}C{-}H}\\ |\\ \mathrm{H{-}C{-}OH}\\ |\\ \mathrm{H{-}C{-}OH}\\ |\\ \mathrm{H{-}C{-}H}\\ |\\ \mathrm{O}\\ |\\ \mathrm{H}\end{array}$$

d-Mannitol

The only difference between these two alcohols, stereoisomerically, lies in the inversion of the group built upon the α-asymmetric carbon atom. Manifestly, stereoisomerism does not explain the whole fact. If some day a strain is found that will react in the opposite manner, *i. e.*, ferment *d*-sorbitol but not *d*-mannitol, new light should be thrown upon the relation of some of the stereoisomers to vital processes.

Bacteria are living chemical reagents. Their life cycle is so short that much more advantageous studies may be made with them than with animals, since experiments may be carried on with bacteria in a few hours which would take years with animals. Up to the present the bacteriologist has found no daylight as he has groped with the ultimate theories of life. As Dr. Kendall expresses it, "Life just seems to be one terrible succession of asymmetric carbon atoms!" The amino acids, as well as the carbohydrates, have the asymmetric carbon atom; this is not so generally true of the fats. An amino acid, or polypeptide of the same composition as those found in the body, with the exception of having the opposite rotatory power, will pass through the intestine unabsorbed as if it were so much sawdust. This is also true of the sugars with reference to bacteria and probably to the human body. What is this connection between the vital processes of life and optical activity? When the rare sugars have made full contribution to science we shall know much more about life than we now comprehend.

ACKNOWLEDGMENT

The author is deeply indebted to Dr. Arthur I. Kendall and Dr. H. E. Redenbaugh, of Northwestern University Medical School, for assistance in the preparation of the bacteriological portion of this paper.

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[1] *J. Infect. Dis.*, **20**, April 4, 1917.

[2] Hulton-Frankel, *J. Inf. Dis.*, **23** (1918), 380.

UNIT WEIGHTS FOR THE PURCHASE OF REAGENTS

By W. D. Collins

Chairman, Committee on Guaranteed Reagents and Standard Apparatus, American Chemical Society

Received October 28, 1920

At the meeting of the Industrial Division of the Society at Chicago, the chairman of the Committee on Guaranteed Reagents and Standard Apparatus presented a brief paper on the subject of uniform unit sizes for the purchase of reagents. A conference with representatives of manufacturers was held in New York at the time of the Chemical Exposition, and the question has since been discussed by correspondence and personally with a number of dealers and large purchasers. As the outcome of these discussions this note has been prepared.

Manufacturers, without exception, have expressed their willingness to furnish reagents in packages of any unit quantity desired by the buyer. The committee feels that if purchasers took full advantage of this policy there would be some increase in cost and in delay in filling orders, as compared with the situation where the number of unit sizes is limited for each reagent.

Use of metric units in chemical laboratory work is almost universal, and certain supplies have long been purchased in metric units. Regular inorganic reagents are at present largely bought by the pound, although the manufacturers are perfectly willing to sell in grams. They list their prices, however, by the pound because nearly all of their orders are in this unit. If members of the Society order reagents by the pound because they are so given in price lists, and manufacturers continue to list the units ordered most, there may be a long period during which the number of orders in metric units is very gradually growing at the expense of the number in pounds.

In order to make this transition period as brief as possible, the unit weights given below are suggested as desirable for the purchase of the reagents named. The regular unit for the greater number of reagents has been the pound. The metric equivalent would naturally be 500 g. Although the saving in expenditure may not be great, there is a certain demand for a smaller unit in laboratories where a few grams of a reagent may be all that is needed in a year. To provide for such needs a package of 100 g. is suggested. Appropriate units for reagents not given in the list can be selected easily from consideration of cost, extent of use, and keeping qualities.

Suggested Unit Weights for Reagents (in Grams)

Acetic Anhydride	200	25	...
Acid:			
Acetic, Glacial	500	100	...
Citric	500	100	...
Hydriodic (1.70)	25	5	...
Hydrobromic (1.38)	100	25	...
Hydrochloric (1.19)	2500[1]	500	...
Iodic	25	5	...
Molybdic	200	25	...
Nitric (1.40–1.42)	3000[1]	500	...
Nitric, Fuming	500	...	...
Perchloric (1.12)	25	...	...
Sulfanilic	25	...	...
Sulfuric (1.84)	4000[1]	500	...
Sulfuric, Fuming	500	...	...
Ammonium Hydroxide	2000[1]	500	...
Ammonium Chloride	500	100	...
Ammonium Oxalate	500	100	...
Ammonium Thiocyanate	200	25	...
Barium Chloride	500	100	...
Benzidine	25	5	...
Bromine	500	200	50
Dimethylglyoxime	25	5	...
Hydroxylamine Hydrochloride	25	5	...
Iodine	500	100	25
Metaphenylenediamine Hydrochloride	25	5	...
Methyl Orange	25	5	...
Methyl Red	5	1	...
Methylene Blue	25	5	...
Phenolphthalein	100	25	...
Phenylhydrazine	25	5	...
Phloroglucinol	10	1	...
Platinum Chloride	5	1	...
Potassium Iodate	100	10	...
Potassium Thiocyanate	200	25	...
Silver Nitrate	100	25	...
Sodium Nitroferricyanide	25	5	...
Sodium Peroxide	100	...	...
Uranium Acetate	100	25	...

[1] The usual 5-pint bottle.

A STUDY OF THE ECONOMIC STATUS OF CHEMISTS IN THE GOVERNMENT SERVICE, TEN EDUCATIONAL INSTITUTIONS, AND THIRTY-SEVEN FIRMS

By Lyman F. Kebler[1,2]

Received October 23, 1920

An Act creating a Commission on Reclassification of Salaries, consisting of three Senators and three Representatives, became effective March 1, 1919. The law directs the Commission to investigate the rate of compensation paid civilian government employees in the District of Columbia, except the navy yard and the postal service, and to report what reclassification and readjustment of compensation should be made so as to provide uniform and equitable pay for the same class and character of work.

The commission consisted of:

Senators: A. A. Jones, *Chairman*, New Mexico; Chas H. Henderson, *Vice Chairman*, Nevada; S. P. Spencer, Missouri.

Representatives: Edward Keating, *Secretary*, Colorado; C. W. Hamlin, Missouri; H. A. Cooper, Wisconsin.

The report was submitted March 12, 1920, and printed as House of Representatives Document 686; 66th Congress, 2nd Session.

The purpose of the investigation was clear. The Commission, as well as Congress, was familiar with the perplexities constantly arising in making appropriations for salaries, and understood in a measure the difficulties confronting the administration heads. It was realized that chaotic conditions existed in the Federal service through lack of any consistent policy for fixing and controlling salaries. It was only after some months of study, however, that the Commission[1] "came to appreciate how seriously the morale of the service had been impaired by the prevalence of unfairness and inconsistency in the compensation of employees."

SECURING DATA REGARDING POSITIONS

In order to secure a complete list and full data regarding positions in the "Washington Service," every person, on April 30, 1919, was required to fill out a detailed questionnaire card which required the approval and signature of the immediate superior and the chief of the bureau or office where the worker was employed. After attaching appropriate class titles to these cards, an almost endless number of valuable tables of facts could be compiled about the positions. One of the chief objects was a classification based on duties and responsibilities. A study of the information collected from various sources showed, among other things, that there was an unduly large number of titles for positions calling for the same or similar qualifications; that a considerable disparity of compensation for the same or similar work often existed; that older, more able and experienced, and better qualified persons longer in the service, often received less compensation than younger recruits of lesser experience, qualifications, and ability; that lack of uniformity in pay scale existed in the several departments; that there was an inequity of salaries to the increase in the cost of living; and "that there is a serious discontent, accompanied by an excessive turnover and loss among the best trained and most efficient employees." The inconsistencies developed clearly showed the impossibility of applying a uniform percentage increase to the basic salaries that would correspond to the increased cost of living. These inequalities and creators of unrest are due to many causes, but the chief ones are lack of employment policy and lack of a basis of adjusting compensation later.

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[1] Member of the Research Staff of the Federal Reclassification Commission.

[2] Data used by permission of the Reclassification Commission.

[1] Commission Report, p. 28.

ADJUSTING TITLES FOR POSITIONS

It should be stated at the outset that this article deals with the chemist primarily, but some of the observations are applicable to the other sciences and even to the clerical forces. There are about seventy titles for government chemists, not including the minor grades. The multiplicity in titles and subtitles is not unique for chemists. Under the designation "Junior Civil Engineer," no less than thirty-three different pay-roll titles were found. The condition simply developed without a guiding hand; no one in particular is blamable.

The exceedingly great difficulty, if not impossibility, of clearly defining this multiplicity and heterogeneity of titles was quite apparent. The titles must be reduced in numbers and simplified. The following general titles for scientific positions were finally agreed on: In chemistry, for example, Junior Aids, Senior Aids, Junior Chemists, Assistant Chemists, Associate Chemists, Chemists, and Senior Chemists. Other features now presented themselves for adjustment. It was claimed by some that the demands for organic chemists were greater than the demands for analytical chemists, and therefore commanded better salaries. This position held sway for some time, not only for the same groups in the same science, but in other sciences as well. For example, it was argued that the demand for chemists was greater than for botanists, and consequently the former commanded and should receive better salaries. Accordingly, separate tentative specifications were outlined for each group in every sub-branch of a science. This required seven specifications for the many subdivisions of chemistry, such as analytical, organic, inorganic, medical, physical, colloidal, metallurgical, mineral, mine, gas, physiological, pharmaceutical, catalytic, etc. A study of the prescribed qualifications of the several groups of the various classes showed how involved the proposed system really was. It neither reduced the number nor simplified the titles. The problem was solved by dropping all but the above seven basic titles for the "Physical Science Service." It was now possible to formulate working specifications for these positions. With this information available, the Commission classified the chemists included in the questionnaire cards. The results with salaries and per cent in each group are given in Table I.

TABLE I

387 Government Chemists in the District of Columbia Classified by the Commission on 1919 Positions, with Salaries and Per cent in Grade

GRADE	NO.	Salaries Minimum	 Maximum	 Average	Per cent in Grade
Junior Aid............	16	720	1200	1164	4.1
Senior Aid............	25	840	1302	1192	6.5
Junior Chemist	89	1000	1860	1419	23.0
Assistant Chemist....	82	1002	2500	1738	21.2
Associate Chemist....	119	1740	4000	2264	30.7
Chemist...............	40	2200	4500	3042	10.3
Senior Chemist.......	16	3000	5000	3904	4.1

SALARY ADJUSTMENTS ON A PRE-WAR BASIS

The very vital question of salaries for the various positions next demanded attention; for compensation, in the final analysis, is the dominant factor. Fixed salaries did not appear to be feasible. The Commission says:[1]

> The Commission recognized the impossibility of deciding on a salary standard that might be considered permanent because of the uncertainty of the cost of living fluctuations. It therefore concluded early in its deliberations to recommend that the salary scale to be submitted to the Congress should be subjected to revision in accordance with any material changes in the cost-of-living figures.

It was recommended that salaries be adjusted on the prewar basis of 1914, by adding a percentage which would enable the employees to maintain the former standard of living. The U. S. Department of Labor reported that the increased cost of living of 1919 over 1914 was 97 per cent. The average advance in salary of members of the Bureau of Chemistry who accepted outside employment from 1914 to 1919, nearly 75 per cent of the force, was, at the time of leaving, 59 per cent, and by the end of 1919 amounted to 75 per cent.

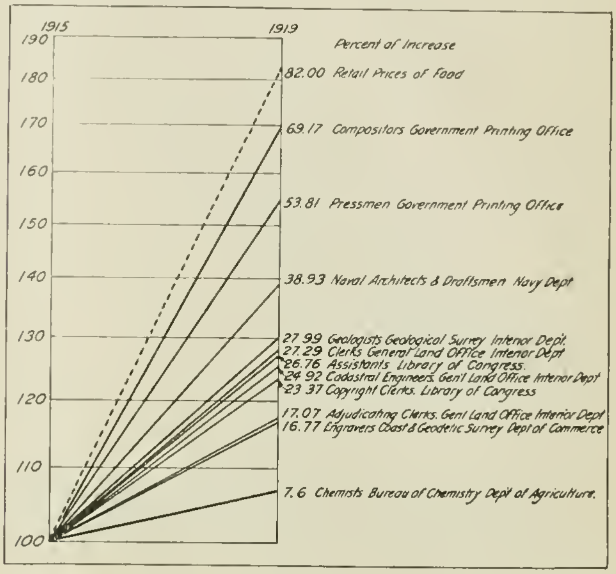

CHART A

Increase, 1915–1919, in Average Salary of Specified Groups of Government Employees Compared with Increase in Retail Prices of Food. Averages Include Bonus (From U. S. Department of Labor, *Monthly Labor Review*, **10** (1920), 31, excepting Bureau of Chemistry Chemists Average).

Charts A and B, based on figures used by the Commission in its work, tell very interesting stories. There were, furthermore, some increases in 1915 over 1914. The great differences in increases, even in the government service for the same or similar work, are striking. One reason given is that certain lines of work are more sensitive to outside market conditions. On referring to Chart B it will be noted that the average increase in salaries of painters, hod carriers, factory employees, railroad employees, and machinists has kept pretty close pace with the increase in the retail prices of food.

The average increase in salary of the scientific force in the Bureau of Chemistry, including the bonus, 1915 to 1919, is 7.6 per cent. The line representing this information was added to Chart A by the writer. One reason for this relatively small percentage increase in the average salary is the fact that less experienced workers at lower salaries were employed when the more experienced and better paid employees resigned.

One difficulty in considering this recommendation was the practical impossibility of collecting sufficient information to serve as a basis for such a computation. In some instances, satisfactory averages were worked out for 1914, but it was discovered that these averages sometimes ran higher than the 1919 averages for the same positions. For a time a flat increase of 80 per cent of the 1914 salaries, after proper adjustments, was under discussion, but nothing definite came of it. Again it was found that to increase the 1914 salaries in proportion to "the increase in the cost of living often produced a figure much in excess

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[1] Commission Report, p. 81.

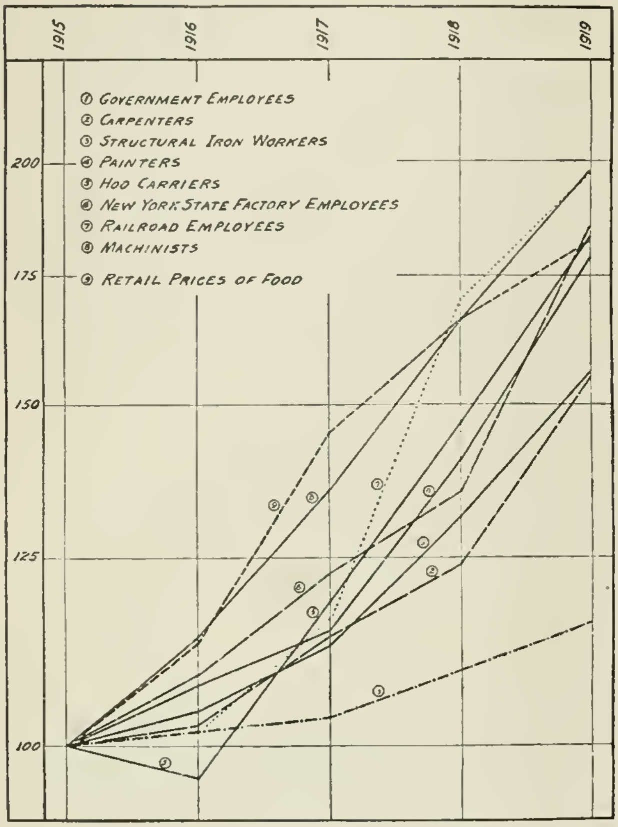

Chart B

Increase, 1915–1919, in Average Salary of Government Employees, Compared with Increase in Retail Prices of Food, Earnings in New York State Factories, and Wage Rates of Certain Skilled and Unskilled Workmen (From U. S. Department of Labor, *Monthly Labor Review*, **10** (1920), 33).

of what outside standards would justify."[1] This does not obtain for chemists covered by the Reclassification Act, as can readily be seen from the data contained in Tables IX, X, and XI.

Tables II and III represent tentative allocation of the 1914 chemical force of the Bureau of Chemistry in Washington, and both in and out of Washington, respectively.

Table II

146 Bureau of Chemistry Workers in the District of Columbia, Classified[1] According to 1914 Positions, Etc.

Grade	No.	Salaries Minimum	Salaries Maximum	Salaries Average	Per cent in Grade
Junior Aid...........	5	600	720	648	3.4
Senior Aid...........	13	720	1200	931	8.9
Junior Chemist......	23	960	1800	1364	15.8
Assistant Chemist....	63	1440	2520	1749	43.2
Associate Chemist....	25	1800	3000	2302	17.1
Chemist.............	10	2760	4000	3226	6.8
Senior Chemist.......	7	3500	5000	3971	4.8

Table III

265 Bureau of Chemistry Force In and Out of Washington, Classified[1] According to 1914 Positions, Etc.

Grade	No.	Salaries Minimum	Salaries Maximum	Salaries Average	Per cent in Grade
Junior Aid...........	6	600	900	690	2.1
Senior Aid...........	13	720	1200	922	4.6
Junior Chemist......	55	1020	1620	1328	19.3
Assistant Chemist....	125	1440	2520	1731	43.9
Associate Chemist....	61	1800	3000	2319	21.4
Chemist.............	15	2760	4000	3317	5.3
Senior Chemist.......	10	3250	5000	3830	3.5

[1] Classified by a member of the Commission's staff and a chemist and a clerk, both many years attached to the Bureau.

Tables IV to VIII, inclusive, give data on salaries, resignations, etc., of chemists in the government service for the years 1914 and 1919, and in part for the intermediary years. Various features contained in these tables will be considered later.

Because of inadequate information, existing unsatisfactory conditions, and the excessive turnover in many services (see Table VII), the Commission decided to send qualified representatives into the field to make a survey of conditions existing in industrial, commercial, and educational organizations with which the Government comes into direct competition, and properly so.

The records[1] of the bureau of employment of the Chemists' Club of New York show an increase in 1919 over 1915 of about

100 per cent in salaries ranging from $1200 to $1500
46 per cent in salaries ranging from 1500 to 1800
460 per cent in salaries ranging from 1800 to 2400
150 per cent in salaries ranging from 2400 to 4000

DATA COLLECTED FROM OUTSIDE ORGANIZATIONS

A list of the firms and educational institutions to be visited was selected by an interdepartmental committee of chemists located in Washington, D. C., and submitted to the Commission for revision and approval. In the final summing up, satisfactory data were procured from thirty-seven firms and ten universities located in fifteen cities, scattered from Washington, D. C., to Buffalo, N. Y., and from Boston to Chicago. The firms included manufacturers of canned goods, coal-tar products, drugs, dyes, electrical supplies, gas mantles, illuminating gas, inks, petroleum products, pure chemicals, rubber goods, and steel; also packers, mail order houses, and commercial laboratories.

The special agents, selected from the Classification and Research Staffs, procured data on 2600 chemists, and classified them in the field according to the Commission's instructions and tentative specifications. The agents naturally did not have as comprehensive a view of the classification work as a whole as did certain members of the research staff who gave attention to all phases of the work. After a conference between the Field Agents and members of the Research Staff, somewhat different, but perfectly satisfactory, allocations were worked out. The results arrived at and the average cash bonus for each class, so far as procurable, are set forth in Table XII. It will be noted that there are some material differences between the two sets of allocations. During the conference it was clearly pointed out that the data, in some cases, were either inadequate or unsatisfactory for inclusion in a work of the character in hand. For example, second-hand information, although undoubtedly correct, was unsatisfactory. Everything admissible had to come through some responsible officer of an organization. Even certain statements coming from accredited officers, of which the following is representative, were eliminated: "Our head chemist receives the same as heads of other departments, about $10,000." Information of the following character was deleted for averages, but recorded separately in the Field Agents' classification: "Fifteen chemists' salaries, $2400 to $4000." Such information can be included in the total make-up, but not in the averages. As a result of the discussion a few of the chemists were also changed from one class to another. For example, in the case of Assistant Chemists, based on the positions held, the Field Agents included salaries ranging from $1600 to $6000. In the Chemists class, the Special Agents grouped workers getting from $3000 to $6000, but the ultimate classification included those getting from $3000 to $10,000. In the case of the Senior Aids, the range from $900 to $1500 was changed to from $900 to $2700.

EMPLOYEES PERMITTED TO FIX OWN SALARIES

The Special Field Agents in this work were chemists. The special members from the Research Staff were not. The criticism was made that the employees were permitted to classify themselves and thus fix their own salaries. A glance at Table XII shows that the Special Agents made less advantageous

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[1] Commission Report, p. 81.

[1] Private communication.

DATA ON SALARIES OF CHEMISTS, CHEMIST'S AIDS, ETC., IN GOVERNMENT SERVICE

TABLE IV

IN SERVICE 1914, GROUPED ACCORDING TO SALARY RANGES

BUREAU OR SUBDIVISION	$720–$1199	1200	1400	1600	1800	2000	2200	2400	2600	2800	3000	3200	3400	3600	3800	4000	4500	4600	4800	5000	6000	TOTAL
Chemistry	5	30	43	48	44	26	18	20	4	..	9	4	5	1	1	6	..	..	..	1	..	265
Animal Industry	3	..	3	..	7	2	1	..	2	1	..	..	..	..	..	1	..	..	..	..	..	20
Soils	..	..	6	2	2	..	..	1	5	..	..	..	..	1	..	..	..	..	..	..	..	17
Plant Industry	..	2	1	1	2	3	2	3	1	..	..	..	..	1	..	..	..	..	..	..	..	16
Public Roads	..	1	1	..	..	1	..	1	..	..	..	..	..	..	..	..	..	..	..	..	..	4
Geological Survey	1	..	..	1	1	1	..	2	..	..	1	..	..	..	..	..	..	..	..	..	..	7
Standards	6	10	4	6	6	2	2	3	1	..	..	..	2	..	..	..	..	..	1	..	..	43
Naval Establishments	1	15	5	4	1	2	2	1	..	..	..	..	..	..	..	..	..	..	..	..	..	31
Patent Office	..	..	6	..	3	5	..	3	4	..	..	..	..	..	..	..	..	..	..	..	..	21
Hygienic Laboratory	..	..	1	..	1	2	..	2	..	..	..	..	..	..	..	..	..	1	..	..	..	7
Mines	14	19	15	4	2	1	..	2	3	..	4	2	..	1	..	1	..	..	1	..	..	69
Internal Revenue	..	..	1	1	..	..	..	1	..	..	1	..	..	..	..	..	..	..	..	..	..	4
Dept. of Agriculture	8	33	54	51	55	32	21	25	12	1	9	4	5	3	1	7	..	..	..	1	..	322
Total Chemists	30	77	86	67	69	45	25	39	20	1	15	6	7	4	1	8	..	1	2	1	..	504

TABLE V—IN SERVICE DECEMBER 1919, GROUPED ACCORDING TO SALARY RANGES

Chemistry	..	4	43	33	33	42	25	24	12	..	9	6	5	2	..	5	1	..	1	..	..	245
Animal Industry	..	1	2	2	6	3	3	2	1	..	1	3	..	..	..	..	1	..	..	..	..	25
Soils	..	..	1	2	1	1	2	2	2	1	..	1	1	..	..	..	..	..	..	..	..	14
Plant Industry	2	2	7	1	5	4	2	3	6	1	..	1	..	1	..	..	..	..	..	..	..	35
Public Roads	..	1	1	1	..	..	2	1	..	..	..	..	..	..	..	..	..	..	..	..	..	6
Geological Survey	..	1	..	..	1	1	..	2	..	..	3	1	..	..	..	..	..	..	..	..	..	9
Standards	4	9	12	12	13	9	1	6	3	..	2	2	3	1	..	1	..	..	1	..	..	79
Naval Establishments	..	..	..	..	..	5	7	3	3	..	4	4	1	4	..	..	..	..	..	..	..	31
Patent Office	..	..	8	..	15	12	1	6	5	..	..	..	..	..	..	..	..	..	..	..	..	47
Hygienic Laboratory	..	1	2	..	1	2	..	2	..	..	2	..	..	..	..	..	..	..	..	..	..	10
Mines	..	1	1	1	3	4	2	1	..	1	1	2	..	1	..	2	..	..	2	..	..	22
Internal Revenue	..	..	..	..	..	..	1	1	..	..	1	..	1	..	..	..	..	..	..	..	..	4
Nitrate Division	..	..	3	5	12	1	6	6	1	..	2	..	..	..	..	..	..	..	..	1	1	38
Dept. of Agriculture	2	8	54	39	45	50	34	32	21	2	10	11	6	3	..	5	2	..	1	..	..	325
Total Chemists	6	20	80	57	90	84	52	59	33	3	25	20	11	9	..	8	2	..	4	1	1	565

TABLE VI—WORKERS WHO REMAINED IN SERVICE FROM 1914 TO 1919, INCLUSIVE, GROUPED ACCORDING TO SALARY RANGES

Chemistry	1	..	1	8	16	28	23	22	11	..	7	5	5	2	..	8	1	..	1	..	..	139
Animal Industry	..	..	2	2	4	3	1	2	..	..	2	2	..	..	..	..	1	..	..	..	..	19
Soils	..	..	..	1	1	..	1	1	2	1	..	1	1	..	..	..	..	..	..	..	..	9
Plant Industry	..	..	2	..	1	2	2	1	5	2	..	..	..	1	..	..	..	..	..	..	..	16
Public Roads	..	..	..	1	..	..	1	..	..	..	..	..	..	..	..	..	..	..	..	..	..	2
Geological Survey	..	..	..	..	1	1	..	1	..	..	3	1	..	..	..	..	..	..	..	..	..	7
Standards	..	..	..	1	..	3	1	3	2	..	1	2	3	1	..	2	..	..	1	..	..	20
Naval Establishments	..	..	..	..	..	5	7	3	3	..	4	4	1	4	..	..	..	..	..	..	..	31
Patent Office	..	..	..	..	1	9	1	5	5	..	..	..	..	..	..	..	..	..	..	..	..	21
Hygienic Laboratory	..	..	..	..	..	1	..	2	..	..	1	..	..	..	..	..	..	..	..	..	..	4
Mines	..	1	1	1	3	4	2	1	..	1	1	2	..	1	..	2	..	..	2	..	..	22
Internal Revenue	..	..	..	..	..	..	1	1	..	..	1	..	1	..	..	..	..	..	..	..	..	4
Dept. of Agriculture	1	..	5	12	22	33	28	26	18	3	9	8	6	3	..	5	2	..	1	..	..	182
Total Chemists	1	1	6	14	27	56	40	42	28	4	20	17	11	9	..	12	2	..	4	..	..	294

TABLE VII—SEPARATIONS FROM BUREAU OF CHEMISTRY, GROUPED ACCORDING TO SALARIES AT TIME OF LEAVING

	Below $1200	$1200	$1400	$1600	$1800	$2000	$2200	$2400	$2600	$3000	$3200	$3500	$3600	$4000	Total	Percentage
1914	2	2	5	1	3	1	2	..	..	..	..	..	1	..	17	6.4
1915	..	2	8	4	1	..	2	1	..	..	..	..	..	..	18	7.1[1]
1916	..	2	3	3	5	2	..	..	..	1	1	..	..	1	19	7.5[1]
1917	3	6	5	5	7	2	2	4	..	..	..	..	..	1	35	13.7[1]
1918	..	4	5	6	10	8	4	1	3	1	1	..	..	1	45	17.6[1]
1919	..	2	13	8	7	9	5	..	3	4	1	1	1	..	54	22.0

[1] Based on average of 1914 and 1919 forces, or 255.

TABLE VIII—PROMOTIONS IN SALARIES OF WORKERS WHO REMAINED IN SERVICE FOR FIVE YEARS (1914–1919)

	Number of Times Promoted										Minimum Total	Maximum Total	Minimum Annual	Maximum Annual	Average Annual
	0	1	2	3	4	5	6	7	8	9					
Chemistry	16	43	46	21	6	4	..	..	..	..	$120	$1200	$ 24	$240	$ 82
Animal Industry	2	3	9	4	4	..	..	..	..	..	180	720	36	144	81
Soils	..	3	5	1	..	..	..	..	..	..	120	750	24	150	87
Plant Industry	5	4	5	2	2	1	..	..	..	..	180	960	36	192	66
Public Roads	..	..	1	1	..	..	..	..	..	..	400	720	80	164	112
Geological Survey	..	2	1	2	..	2	..	..	..	..	120	1020	24	204	118
Standards	1	2	2	3	3	5	3	1	..	..	400	1600	80	320	175
Naval Establishments	..	..	..	3	6	11	7	3	..	1	625	2025	125	405	251
Patent Office	9	5	7	..	..	..	..	..	..	..	50	840	10	168	54
Hygienic Laboratory	1	1	2	..	..	..	..	..	..	..	500	1000	100	200	110
Mines	1	1	3	7	6	3	1	..	..	..	200	1680	40	336	141
Internal Revenue	..	2	..	2	..	..	..	..	..	..	500	900	100	180	138

allocations for themselves than did the non-chemist members of the Research Staff. In regard to the charge that the employees classified themselves, the Commisssion says:[1]

> The classification experts with whom we consulted warned us that it was essential that we gain and retain the confidence of the employees affected by our work.
>
> Your Commission has had no secrets to conceal. We were engaged in a public work and we were all agreed that the best way to avoid misunderstandings was to conduct our inquiries in such an open, above-board fashion that everyone interested might know not only our conclusions but the processes by which these conclusions were reached.
>
> In justice to the employees it should be stated that the most careful scrutiny of the members of the Commission and its specialists has failed to reveal a single instance where an employee detailed to our Commission has even attempted to use the opportunity thus afforded to bring about a result inimical to the public interest.

FEATURES ESSENTIAL IN DETERMINING COMPENSATION

So far our observations have been centered around salaries, but in determining compensation or a wage policy, other elements must be and were taken into consideration, such as recent and contemplated salary increases, the working environments, privileges, restrictions, equities, bonuses, insurance, profit sharing, pensions, health provisions, etc. Some of the advantages and disadvantages obtaining in one or more of the government departments are pointed out by the Commission and are in substance as follows:

ADVANTAGES—A 7-hr. work day; comparative security and permanency of tenure; 30 days each sick and annual leave, generously administered, although discretionary with the heads of departments, and some bureaus do not grant any sick leave; an annual bonus of $240 for salaries up to and including $2500;

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[1] Commission Report, p. 15.

greater freedom for some to engage in research work than that given by many commercial organizations.

DISADVANTAGES—Inadequate living wage to meet the high cost of living; unequal entrance salaries for the same work; no plan for pay increases as usefulness increases; stagnation in salaries; "red tape" restricting individual initiative and originality, which is particularly distasteful and deadening to professional workers; written consent for doing any outside work (such as teaching in any educational institutions, publishing articles on any subject, writing books, either gratis or for compensation); refusal to grant leave for employees to study at educational institutions; limited opportunities for advancement compared with progressive industrial practice; forbidden to teach in any institutions giving preparatory work for civil service examinations; forbidden to indulge in any political activity or express views publicly on political subjects; employees on account of the appointment law are "foreigners" in Washington, and are required to establish themselves at a high living cost, high transportation expenses to return home for voting and other purposes; lack of opportunity for healthy recreation and social intercourse; inadequate eating facilities for half-hour lunch period; scant health provisions; inadequacy of a $4.00 per diem allowance, based on the 1914 law, for subsistence while traveling on official business, and the necessity of the employees paying the unavoidable increases out of their own meager salaries; lack of any thorough safety program; no provisions for retirement. (Retirement law passed since Commission's Report.)

Before leaving the above, permit me to quote a few of the Commission's observations:[1]

> In general, there should be as little regulation as possible of employees' activities, literary and otherwise, outside of office hours. Aside from matters connected with the official work of the employee, such restrictions are for the most part unnecessary and humiliating. Moreover, if adequate compensation is provided for an employee's official work, there is little danger of his carrying outside work to the point where it will really detract from his efficiency. The comparatively few cases of this sort, as well as of indiscretion, can be dealt with more effectively as they arise, than by attempting to prevent them through restrictive regulations, the chief effect of which is to lower the morale of the entire force.
>
> Finally, every effort should be made to stimulate initiative and originality on the part of scientific and other professional workers. It is peculiarly appropriate that the Federal Goverment should take the lead in research work of all kinds, but it cannot do so unless it is able to attract and retain independent thinkers of the highest type. The reduction of red tape to the minimum, the encouragement of freedom of thought and action to the maximum, and the direction of research by thoroughly trained investigators would all assist to make this possible.

The Special Agents were requested to procure data on all matters considered above and others from the educational institutions and the industries visited. Many were known in a general way but required verification. The following general summaries include the essential features found in one or more, but not necessarily all of the different organizations visited. The observations here recorded are and must of necessity be relative to some extent, and some readers may disagree with some of the grouping.

EDUCATIONAL INSTITUTIONS

ADVANTAGES—Comparative security and permanency of tenure; usually attractive environments; assured social and scientific prestige; few embarrassing and irritating restrictions; flexibility and freedom of time; few fixed hours of work; liberal vacation periods in which to study, recuperate, prosecute research work, write, enhance one's income, etc.; a Sabbatical year with half pay; no limits as to sick leave (One official interviewed said: "Sickness is not a choice but a necessary evil, and we do not put any limit on it"); freedom to use the laboratory facilities; abundant recreational facilities; freedom to patent inventions and enjoy royalties (government workers are forbidden to profit financially by patenting new discoveries); freedom to engage in politics; limited insurance provided free or at reduced rates; retirement at a certain age on half maximum salary (An employee of the city of Philadelphia may retire at the age of 60 and upwards, after having been employed for 20 or more years, and receive 50 per cent of his average salary during the past 5 years of employment, not to exceed $100 per month, in weekly payments the remainder of his life. For this privilege he contributes 2 per cent of his monthly salary, not to exceed $4.00 per month); increases in salaries from 25 to 50 per cent; comparative freedom to engage in expert or consultation work. (Such work is officially encouraged by some institutions, not merely for the purpose of increasing their prestige, but also as tending to keep the professors in closer touch with the commercial phases of their subjects, thus enhancing their value as teachers. Consultation work in one institution varied from $725 per annum to $15,000. In fact, the teaching position is looked on by some as a sort of a retainer's fee. One Board of Health urges its employees to engage in some teaching of their special subjects for the purpose of "keeping them on their toes.")

DISADVANTAGES—A generally inadequate living wage to meet the high cost of living. (For this reason many are leaving teaching to engage in commercial work.) Some would here class the distasteful routine features of certain teaching, but this is paralleled in some form in every vocation of life.

THE INDUSTRIES

ADVANTAGES—Generally the best salaries and substantial raises (one firm's rate of increase per year is $300 for employees receiving up to and including $3000, and about $600 for all above $3000. A chemist was on the pay roll of the Bureau of Chemistry nearly five years and was then getting $1620 per annum; he resigned to accept a $5000 job and three years later was getting $25,000); certainty of profiting if the employee makes good; enjoyment of royalties and bonuses on improvements, discoveries, patents, etc.; free insurance from $500 to $5000; a "Safety First" program (the death rate due to accidents in the Government, during the first 10 months of 1919, was higher than that of so hazardous an industry as mining);[1] retirement at 65 to 70 after serving from 15 to 25 years, with income ranging from 50 to 75 per cent of salary, and varying from $1200 to $5000 annually as maximums; profit sharing varying from 5 to 100 per cent of previous year's salaries, depending on actual accomplishments, mental attitude, and financial status of firms; participation in stock purchasing at par on the installment plan; disability compensation (one firm pays married persons two-thirds of regular salary and single ones one-half for a period of 52 weeks; meals at cost; medical and dental service free or at cost. (In the Government "scant provision is made for medical and surgical relief"); liberal recreational facilities provided either free or at cost (scant recreational facilities in Government); purchasing supplies on contracts of firms; providing employees food and clothing at cost; freedom to engage in political activity; freedom to teach, talk or write on any subject not a business secret or confidential in nature on own time.

DISADVANTAGES—Less social and scientific prestige; less favorable surroundings; longer hours (average: industries 44 per week, Government 41); more intensive application (this is open to debate and if true obtains only in some cases. Application is generally reflected by success attained); consideration of direct financial returns; less annual vacation (on this point the Commission, on comparing the leave of the industries and the Government, says: "The total amount that is granted in the two services is approximately the same"); no sick leave (many Federal employees do not get any. On the question of sick leave in the industries, the general reply was: "We have no fixed policy, but our salaried employees are taken care of").

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[1] Commission Report, p. 100.

[1] Commission Report, p. 103.

With the information now available the Commission adopted specifications for chemists, classified the positions, and outlined schedules of compensation for the respective classes, which are as follows:

SPECIFICATIONS

Title of Class—Junior Aid in Chemistry

Specifications of Class

Duties: To assist chemists in the performance of routine laboratory work; and to perform related work as required.

Examples—Caring for chemicals and apparatus; assisting in the construction of apparatus for chemical work; caring for and feeding laboratory animals used in chemical nutrition experiments; making solutions; performing simple routine analyses.

Qualifications—Training equivalent to that represented by graduation from high school, including one year of chemistry and one year of physics; accuracy and carefulness.

Principal Lines of Promotion

To: Senior Aid in Chemistry

Compensation for Class

Annual: $840–$900–$960–$1020–$1080–$1140–$1200

Title of Class—Senior Aid in Chemistry

Specifications of Class

Duties: To assist chemists in the performance of chemical work, or to make routine chemical analyses, and to perform related work as required.

Examples—Constructing apparatus for chemical operations; making routine analyses such as determining the ultimate composition of organic compounds, determining the ash and moisture contents of animal and vegetable products, or making nitrogen and sulfur determinations; assisting in chemical investigations.

Qualifications: Training equivalent to that represented by graduation from high school, and by not less than 2 yrs. college work, including at least fifteen college credits in chemistry; accuracy and carefulness.

Principal Lines of Promotion

From: Junior Aid in Chemistry
To: Junior Chemist; Junior Metallurgist

Compensation for Class

Annual: $1200–$1320–$1440–$1560–$1680–$1800

Title of Class—Junior Chemist

Specifications of Class

Duties: To perform, under immediate supervision, routine work in chemistry; and to perform related work as required

Examples—Making routine determinations in analyses of ores, alloys, soils, fuels, paints, insecticides, water, beverages, and foodstuffs; preparing material used in nutrition experiments; assisting in the isolation and analysis of proteins; synthesizing simple organic compounds; measuring the solubility of chemical compounds; performing routine measurements of the hydrogen-ion concentration of solutions; assisting in the construction and operation of apparatus for chemical manufacturing on a small scale; serving as an observer in chemical plant performance tests; making tests for the control of operations in industrial chemistry; preparing reagents and solutions for use in analyses; constructing simple apparatus.

Qualifications: Training equivalent to that represented by graduation with a degree from an institution of recognized standing, with major work in chemistry, including general inorganic, analytical, and organic chemistry; additional training in one or more of the following optional lines: Biological, dairy, engineering, explosives, food, fuel, inorganic, metallurgical, organic, petroleum, pharmaceutical, physical, or soil chemistry; ability to read scientific French or German; and initiative.

Principal Lines of Promotion

From: Senior Aid in Chemistry
To: Assistant Chemist

Compensation for Class

Annual: $1800–$1920–$2040–$2160

Title of Class—Assistant Chemist

Specifications of Class

Duties: To perform, under supervision, either individually or with the assistance of subordinates, general work in chemistry; and to perform related work as required.

Examples—Preparing indicators for special work; ascertaining the degree of ionization of acids, bases, and salts; studying the setting of gels determining yields in chemical processes; conducting simple industrial chemical investigations; supervising control operations in industrial plants; isolating organic compounds from plant and animal tissues; preparing special reagents for work in biological chemistry; isolating proteins and ascertaining their chemical and physical properties; performing digestion experiments, including the control of nitrogen balance; making independent analyses of ores, alloys, soils, fuels, paints, insecticides, water, beverages, and foodstuffs; determining the purity of chemical reagents; determining the fineness of bullion used in coinage; performing electroanalyses of silver, copper, zinc, and other metals; studying methods for the assay of pharmaceutical products; determining the strength and purity of medicines; determining accuracy of the compounding of prescriptions; analyzing official samples of food or drug products as a basis for determining the necessity for federal prosecution under the Food and Drugs Act; appearing as analyst witness in cases involving violations of the Federal Food and Drugs Act.

Qualifications: Training equivalent to that represented by graduation with a degree from an institution of recognized standing, with major work in chemistry, including general inorganic, analytical, and organic chemistry and by not less than two years graduate work in one or more of the following optional lines: agricultural, analytical, biological, dairy, engineering, explosives, food, fuel, inorganic, metallurgical, organic, petroleum, pharmaceutical, physical, or soil chemistry; ability to read scientific French and German, and to prepare chemical manuscripts in clear and concise English; and initiative.

Principal Lines of Promotion

From: Junior Chemist
To: Associate Chemist

Compensation for Class

Annual: $2400–$2520–$2640–$2760–$2880–$3000

Title of Class—Associate Chemist

Specifications of Class

Duties: To perform under general direction, either individually or with associates or subordinates, specialized work in chemistry which may or may not involve supervisory duties; and to perform related work as required.

Examples—Studying the relations between the chemical composition and the physical properties of ferrous and non-ferrous alloys; planning and supervising industrial chemical investigations; drafting general specifications for the design of chemical plants; studying the availability and utilization of raw materials and finished chemical products; conducting field investigations of chemical plants and processes; controlling yields in chemical processes; ascertaining the properties of emulsions; applying crystallographic methods to chemical analyses; perfecting methods for preparing organic compounds such as color intermediates; synthetic pharmaceuticals, photographic chemicals, and coal-tar derivatives; determining the structure of organic compounds; isolating and identifying organic compounds from plant and animal tissues; isolating and investigating toxic substances from plants and animals, conducting nutrition experiments to determine the relative food value of various proteins; isolating and identifying organic compounds from soils; devising new analytical methods; testing the accuracy of existing methods; determining the ingredients in patent medicines and secret remedies; preparing reports to be used as evidence, and appearing as expert witness in cases involving violations of the Federal Food and Drug Act, Internal Revenue, or other Federal laws.

Qualifications: Training equivalent to that represented by graduation with a degree from an institution of recognized standing, with major work in chemistry, including general inorganic, analytical and organic chemistry, by not less than 3 yrs. graduate work, and by one year's professional experience, in one or more of the following optional lines: Agricultural, analytical, biological, dairy, engineering, explosives, food, fuel, inorganic, metallurgical, organic, petroleum, pharmaceutical, physical, or soil chemistry; ability to read scientific French and German, and to prepare for publication, in clear and concise English, manuscripts embodying the results of chemical investigations; and proved technical and scientific proficiency.

Principal Lines of Promotion

From: Assistant Chemist
To: Chemist

Compensation for Class

Annual: $3240–$3360–$3480–$3600–$3720–$3840

Title of Class—Chemist

Specifications of Class

Duties: To perform one or more of the following functions: (1) To carry on, either individually or with associates or subordinates, highly specialized lines of chemical research; (2) to act in a consulting or advisory capacity on problems in chemistry; (3) to plan and execute major lines of chemical work; or (4) to perform major administrative work under executive direction; and to perform other related work.

Examples—Planning and conducting the more advanced and difficult chemical investigations; planning and directing the work of staffs of investigators; furnishing expert advice to the various government agencies; conducting research to obtain information for establishing or improving important industrial processes for the general public welfare as provided for in specific enactments by Congress; planning and directing chemical work essential to the enforcement of laws enacted by Congress; coordinating chemical and related work to increase the efficiency of investigations requiring the coöperation of government establishments and important industries.

Qualifications: Training equivalent to that represented by graduation with a degree from an institution of recognized standing, with major work in chemistry, but not less than 3 yrs. graduate work in chemistry and by not less than 4 yrs. professional experience of which at least 3 yrs. shall have been in work of the grade required of an Associate Chemist; proven ability to carry on or to direct research work in chemistry; ability to read scientific French and German, and to prepare for publication, in clear and concise English, manuscripts embodying the results of chemical investigations.

Principal Lines of Promotion

From: Associate Chemist

To: Senior Chemist; Assistant Chief, Bureau of Chemistry; Chief, Bureau of Chemistry

Compensation for Class

Annual: $4140–$4320–$4500–$4680–$4860–$5040

Title of Class—Senior Chemist

Specifications of Class

Duties: To perform one or more of the following functions: (1) To carry on or direct the most difficult and comprehensive lines of advanced chemical investigations; (2) to act as consulting specialist in the field of chemistry; or (3) to perform major administrative work involving the broadest lines of policy; and to perform other related work.

Examples—Assuming responsibility for the most exacting and intricate chemical investigations; deciding questions of policy involving chemical standards for commercial products; directing groups of workers on major chemical projects; serving as chief of an important chemical division of a bureau.

Qualifications: Training equivalent to that represented by graduation with a degree from an institution of recognized standing, with major work in chemistry, but not less than 3 yrs. graduate work in chemistry, and by not less than 8 yrs. professional experience, of which at least 3 yrs. shall have been in work of the grade of Chemist; large capacity and proven ability to perform, direct, or administer work in the most difficult and comprehensive lines of chemistry.

Principal Lines of Promotion

From: Chemist

To: Assistant Chief, Bureau of Chemistry; Chief, Bureau of Chemistry

Compensation for Class

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DISCUSSION OF TABLES

The accompanying tables lend themselves to extended discussion and a multitude of deductions. It is proposed to call attention here to only a few of the salient features. Table III is included for the reason that the Bureau of Chemistry force outside of Washington is an integral part of the Bureau. The average salary paid chemists outside of Washington is about $93 less than the average paid in Washington. It would be manifestly unfair to increase salaries in Washington and neglect the outside force.

Certain subdivisions, represented by Tables IV, V, and VI, include Washington workers only, others out-of-Washington employees, and some include both. Tables IV and V show that there have been some unequal upward revisions of salaries, from 1914 to 1919, inclusive. In 1914 nearly one-half of the chemists in the Naval Establishments received $1200, while in 1919 none were paid less than $2000. The 1919 figures do not include the annual bonus.

The factors underlying the increases differ in various organizations; in the Bureau of Internal Revenue there is the enforcement of the recent Prohibition and the Anti-narcotic Laws; in the Patent Office we find the difficulties of filling the lower paying statutory positions, rendered vacant by resignations. The increases in the Naval Establishments are due to several factors; first, they represent war expanded units, and, second, the close relation existing between these chemists and other groups of workers in the Navy Department. The war brought about a great demand for workers in shipyards, with resultant keener competition and the shifting of these employees from yard to yard. A committee was appointed, of which V. Everit Macy was chairman, to adjust the problems, keeping in mind "general and material increases in the cost of living." The report of the committee is commonly known as the "Macy Award," and covers the employees of privately owned shipyards working for the Government. The Macy Award represents material enhancements in salaries. The increases were later passed on to chemists in the Naval Establishments through the "Henry Award." The "Henry Award" prescribes higher qualifications for the various groups of workers than does the Macy Award. The Henry Award became effective in July 1919, and provides the following compensation: Chemists, $7.60 to $12.00 per diem, and Assistant Chemists $5.20 to $7.20 per diem. Promotions are made in the increment of 40 cents per diem.

The Nitrate Division was created during the war and therefore shared in proportionately higher salaries. The director of this division receives a higher salary than any other civilian government chemist.

Table VII shows the resignations from the Bureau of Chemistry from 1914 to 1919, inclusive. The percentage of those resigning receiving the higher salaries, $3000 and above, is nearly equal to the percentage resigning receiving salaries below $3000.

Table VIII covers increases in salaries from 1914 to 1919, inclusive. The increases are exclusive of the bonus. Those not receiving an increase are not included in the totals and averages. The average annual increase, exclusive of those who did not receive an increase, varies from $54 in the Patent Office to $251 in the Navy Establishments. During these five years of material increase of living, 12 per cent of these workers did not receive any increase in salaries but material increases were made in a number of bureaus. In the Naval Establishments all salaries advanced and one chemist's salary was increased nine times.

Table IX

105 Chemists of 10 Educational Institutions, Classified According to Positions Held at End of 1919 Calendar Year

Grade	No.	Salaries Minimum	Salaries Maximum	Salaries Average	Per cent in Grade
Junior Aid..........	6	720	720	720	5.7
Senior Aid..........	6	900	900	900	5.7
Junior Chemist......	25	1250	2400	1908	23.8
Assistant Chemist....	15	2000	3500	2878	14.3
Associate Chemist....	27	1800	4500	2991	25.7
Chemist............	20	3000	6125	4975	19.1
Senior Chemist.......	6	5000	8000	5650	5.7

Table X

1372 Chemists of 37 Firms and 10 Educational Institutions Located in 21 Cities, Classified According to Positions Held at End of 1919 Calendar Year

Grade	No.	Salaries Minimum	Salaries Maximum	Salaries Average	Per cent in Grade
Junior Aid..........	149	720	1664	1254	10.9
Senior Aid..........	16	900	2700	1589	1.2
Junior Chemist......	638	1080	3000	2062	46.4
Assistant Chemist....	239	1600	6000	3334	17.4
Associate Chemist....	130	1800	6000	3888	9.5
Chemist............	163	3000	10000	6758	11.9
Senior Chemist.......	37	5000	15000	10138	2.7

Table XI

Comparison of Average Salaries of Chemists in the Washidgton Service, the Educational Institutions, and Industries Included in the Above Tables

Group	Chemists in Washington Covered by the Reclassification Act	Chemists in 10 Educational Institutions	Chemists in 37 Firms and 10 Educational Institutions	Percentage Difference between Salaries of Government and Educational Chemists	Percentage Salary Increases of Chemists in 37 Firms and 10 Educational Institutions over Government Chemists
Junior Aid..........	1164	720	1254	38.1—	7.7
Senior Aid..........	1192	900	1589	24.5—	33.3
Junior Chemist......	1419	1908	2062	34.4+	45.3
Assistant Chemist....	1738	2878	3334	65.6+	91.8
Associate Chemist....	2264	2991	3888	32.1+	71.7
Chemist............	3042	4976	6758	63.5+	122.2
Senior Chemist.......	3904	5650	10138	44.7+	159.5

Tables IX, X, and XI give a clear picture of salaries. Omitting Junior and Senior Aids, the increases shown in Table XI over comparable Government Chemists, in cases of the educational institutions, varies from 32 to 65 per cent, and in case of chemists in all organizations from 45 to 159 per cent.

Table XII

		Tentative Allocation by Special Agents in the Field					Final Allocation after Conference of Special Agents and Research Staff of Commission			
		Definite Salaries			Salary Ranges					
Titles	Total No.	No.	Min.	Max.	No.	Ranges	No.	Min.	Max.	Cash Bonus
Junior Aid	149	131	720	1664	18	728 1664	149	720	1664	160
Senior Aids	62	43	900	1500	19	960 2100	16	900	2700	....
Junior Chemists	1127	957	1080	3000	170	1200 2500	638	1080	3000	309
Assistant Chemists	863	795	2000	4500	68	1920 4000	239	1600	6000	488
Associate Chemists	180	148	1800	5500	32	3000 6000	130	1800	6000	436
Chemists	180	168	3000	6000	12	4800 10000	163	3000	10000	1125
Senior Chemists	39	39	5000	15000	..	.....	37	5000	15000	1085

It will be noted that the percentage of Senior Chemists in Table X is much lower than the percentage for senior chemists in any other allocation. This is due to the fact that it was generally impossible for the field agents to get the compensation of the highest salaried employees. On this point note what one Chemical Director says:

> I would state that the average salary of nine men in our company, who compare with the grade of senior chemist, is $11,013. These men are the heads of our research laboratories, and of divisions of the chemical departments, but do not include the chemical director. It would be impractical to use salaries of chemists in the manufacturing departments, as while most of our plant superintendents began as chemists, the majority of the better men are now occupying positions of great responsibility as managers of departments, vice presidents, and directors of the company, etc. While the fact that they occupy such positions is undoubtedly due to their chemical training, yet their present duties are not chemical except in the most general way.

The head of another firm writes:

> I cannot give you the information you desire in reference to my own salary.
>
> I will gladly give you information regarding the salaries of three chemists in our employ:
>
> A—Over $15,000.00
> B—Over 12,000.00
> C—Over 5,200.00
>
> One of the above chemists was formerly in the employ of the United States Government, but left government employ on account of his compensation.
>
> Considering chemists as a class, it is my opinion that with few exceptions, in general industries really remarkably good chemists are underpaid.

Since collecting the data for the Reclassification Commission, material increases of salaries have been reported by a number of organizations, but Congress has not as yet given any relief to the civilian scientific government workers.

NOTES AND CORRESPONDENCE

AN OPPORTUNITY TO OBTAIN THE LONDON CHEMICAL SOCIETY'S ANNUAL REPORTS ON THE PROGRESS OF CHEMISTRY AT A REDUCED RATE

Editor of the Journal of Industrial and Engineering Chemistry:

To care for the desire on the part of a good many American chemists for critical reviews of the new chemistry published during appropriate periods of time it was thought better by the Council of the American Chemical Society to endeavor to arrange for a wider distribution in this country of the excellent annual reviews published by the London Chemical Society than to attempt to publish such reviews independently. In accordance with the wish of the Council of our Society I placed our request before the Council of the London Society and, as anticipated, this body has again shown the same splendid spirit of coöperation as has characterized other dealings. The London Chemical Society is willing to send copies of its Annual Reports for 1920 to members of the American Chemical Society for 7 shillings per copy, a rate which is less than that charged to the general public. This covers postage. Anyone who wishes to take advantage of this opportunity is to send his order, together with a remittance for 7 shillings, made payable to S. E. Carr, to the Assistant Secretary, Chemical Society, Burlington House, Piccadilly, London, W. 1, England, so that it will reach him by January 1, 1921. It is unfortunate that the time limit is so near at hand, but arrangements could not be completed sooner and it is necessary for the Chemical Society to know the number of copies desired by January 1 in order to know how many copies to print. Each applicant should state that he is a member of the American Chemical Society.

To those not familiar with the Annual Reports on the Progress of Chemistry, it is explained that they appear in the form of a book, well bound, which is divided into chapters relating to different branches of chemistry, each of which is written by a chemist of high standing. References to original papers are given, and author and subject indexes are provided. These reviews, since they furnish continuous reading and since they are of a critical nature, serve as a most interesting, convenient and valuable means by which one can refresh his memory or become informed as to the more important advances in chemistry during the period covered.

E. J. Crane

Columbus, Ohio

SEMI-CENTENNIAL EXERCISES AT OHIO STATE UNIVERSITY

In connection with the Semi-Centennial Exercises of the Ohio State University, the Department of Chemistry held a chemical conference of its graduates on October 16, 1920. This conference was attended by a large number of the alumni of the University. The speakers were all graduates of the Department. The program was as follows:

1—A Brief History of the Department of Chemistry. William McPherson, Head Department of Chemistry, Ohio State University.
2—The Organization of a Chemistry Department. Winfred F. Coover, Professor of Chemistry, Iowa State College, Ames, Iowa.
3—A Chemical Attack upon the Unsolved Problem of Human Diabetes. Edgar J. Witzemann, Research Chemist, Sprague Memorial Institute, Rush Medical College, University of Chicago, Chicago, Ill.
4—Problems in the Petroleum Industry. George A. Burrell, President, The Gasoline Recovery Co., 2907 Equitable Bldg., New York City. (Formerly Colonel C. W. S., U. S. A.)
5—The Composition of Automobile Exhaust Gas in Reference to the Ventilation of Vehicular Tunnels. Arno C. Fieldner, Research Chemist, Bureau of Mines, Pittsburgh, Pa. (Formerly Major C. W. S., U. S. A.)

NEWS ITEMS FROM THE NATIONAL RESEARCH COUNCIL

An international conference to consider the future of the International Catalogue of Scientific Literature has just been held in London at the invitation of the Royal Society. Representatives were present from fourteen countries.

Up to the time of the war, more than thirty countries were joined in undertaking the indexing and publishing of the index of the scientific literature of the world. Fourteen annual issues, each of seventeen volumes, have been published covering the literature from 1901 to 1914. The results of the war, together with the much-increased cost of printing and publishing, have interrupted the undertaking, and no index of scientific literature published since 1914 has been issued. The conference decided that even though a change may be made in the future in the method of indexing and of publishing the index, as has often been suggested, it is imperatively necessary to continue the present method until the scientific literature published up to the end of 1915 and possibly also that up to the end of 1920 has been catalogued.

A site for the new building in Washington which is to serve as a home for the National Academy of Sciences and the National Research Council has recently been obtained. It comprises the entire block bounded by B and C Streets and Twenty-first and Twenty-second Streets, N. W., and faces the Lincoln Memorial in Potomac Park.

DEPARTMENT OF ENGINEERING RESEARCH AT THE UNIVERSITY OF MICHIGAN

Public announcement has recently been made of the opening of the new Department of Engineering Research at the University of Michigan. This department is to be at the service of the industries of the state for the solution of their various problems.

The department will be entirely under the control of the Board of Regents of the University, and any results obtained in the university laboratories may be published at the discretion of the Board. The administration of the department is placed in the hands of a director, who is a member of the Faculty, and an administrative committee, consisting of the dean of the Engineering College, and the heads of the professional departments of the College of Engineering. An advisory board of one hundred members, made up from the leading manufacturers of the state, will act on questions of policy, through its executive committee.

The University has made an appropriation of $10,000 to defray the expenses of the central office, but otherwise the department must be self-supporting. The director is Professor Albert E. White, who is in charge of metallurgical work at the University.

Many requests for service along various lines of research have already come in. The advisory committee is already organized, and there is no doubt that the biggest manufacturers of the state are behind the undertaking.

AMERICAN FIELD SERVICE FELLOWSHIPS FOR FRENCH UNIVERSITIES

The American Field Service Fellowships for French Universities, formerly the Society for American Fellowships in French Universities, has been formed to award to American students fellowships for advance study in France, as a memorial to the men of the American Field Service who died in France.

Fellowships for 1921–22, not to exceed 25, will be of the value of $200 plus 10,000 francs, and are renewable for a second year. Fellowships are offered in various fields of science, art, languages and literature, engineering, law, economics, and philosophy, and in universities at Paris, Aix-Marseille, Alger, Besançon, Bordeaux, Caen, Clermont-Ferrand, Dijon, Grenoble, Lille, Lyon, Montpellier, Nancy, Poitiers, Rennes, Strasbourg, and Toulouse.

The opportunities afforded in French universities are described in "Science and Learning in France," issued in 1917 with the collaboration of one hundred American scholars by the Society for American Fellowships in French Universities, copies of which were sent to the libraries of every college in the United States. Copies may be obtained at one dollar each from the editor of "Science and Learning in France," 31 West Lake St., Chicago, Ill.

Applications for fellowships should be made to the Secretary, Dr. I. L. Kandel, 576 Fifth Ave., New York City.

WASHINGTON UNIVERSITY

The Chemistry Department of Washington University, St. Louis, Mo., has greatly increased its facilities by adding to Busch Hall a new laboratory for quantitative analysis to accommodate 100 students, and a new additional laboratory for general chemistry to accommodate 168 students.

SOCIETY OF MECHANICAL ENGINEERS

At the invitation of the Society of Mechanical Engineers, Mr. A. C. Fieldner has been appointed by President W. A. Noyes as the official representative of the American Chemical Society at the meeting of the Fuel Section at the annual meeting in New York City, December 7 to 10, 1920. A cordial invitation has been extended to any member of the American Chemical Society who may be interested to attend the session.

THE JELLY STRENGTH OF GELATINS AND GLUES—CORRECTION

In our paper under the above title [This Journal, 12 (1920), 1007] Fig. 8 was incorrectly lettered in the original drawing. The legend for the *y*-axis of the graph should read: *Tensile Strength in Grams*, not Tensile Strength in Lbs./Sq. In.

S. E. Sheppard, S. Sweet and J. Scott, Jr.

Rochester, N. Y.

GASOLINE FROM NATURAL GAS. IV—TEMPERATURE CORRECTION AND BLENDING CHARTS—CORRECTION

In the article of the above title [This Journal, 12 (1920), 1011], the following revisions should be made in Table II:

Observed Gravity ° Bé.	Temperature ° F.	Degrees Baumé at 60° F.
69	8	76.7 in place of 75.7
79	— 8	90.8 in place of 89.8
79	— 6	90.4 in place of 89.4
79	— 4	90.0 in place of 89.0
87	—18	102.4 in place of 103.4

In Table III typographical errors should be corrected as follows:

Observed Gravity ° Bé.	Temperature ° F.	Correction Factor
90	110	0.9610 in place of 0.9630
90	100	0.9685 in place of 0.9605

R. P. Anderson

Oil City, Pa.

RELATIONSHIP OF HYDROGEN-ION CONCENTRATION OF NATURAL WATERS TO CARBON DIOXIDE CONTENT—CORRECTION

In the paper on the above subject [This Journal, 12 (1920), 989] the following changes should be made:

On page 990, Equation 3 should read:

$$(H_2CO_3 + CO_2) = 3.333 \times 10^{-2} \times (HCO_3^-)$$

and five lines below Equation 3 the similar expression should be:

$$(CO_2) + 3.333 \times 10^{-2} \times (HCO_3^-)$$

R. Edman Greenfield

Urbana, Illinois

CALENDAR OF MEETINGS

American Institute of Chemical Engineers—Winter Meeting, St. Charles Hotel, New Orleans, La., December 6 to 9, 1920.

American Society of Mechanical Engineers—Annual Meeting, 29 W. 39th St., New York, N. Y., December 7 to 10, 1920.

American Association for the Advancement of Science—Annual Meeting, Chicago, Ill., December 27, 1920, to January 1, 1921.

American Ceramic Society—Annual Meeting, Deschler Hotel, Columbus, Ohio, February 21 to 26, 1921.

American Electrochemical Society—Spring Meeting, Hotel Chalfonte, Atlantic City, N. J., April 21 to 23, 1921.

American Chemical Society—Sixty-first Meeting, Rochester, N. Y., April 26 to 29, 1921.

WASHINGTON LETTER

By J. B. McDonnell, Union Trust Building, Washington, D. C.

THE DYE BILL SITUATION

Congress will be back in harness within a few days after this letter is published and during the short session which will end the life of the present Congress in March, it will be determined whether or not the dye industry is to be given protection to supplant the temporary barrier now in place, without a delay of several months.

Except for slowing up investments in new, and enlargement of old plants, delay in enactment of legislation to protect the industry has had little effect up to this time, because during the continuation of the technical state of war with Germany, it was possible to continue the protection afforded the industry under the war legislation empowering the War Trade Board to restrict imports. Ending of this technical state of war, however, is a prospect of the next few months. Peace will be brought about in some fashion in the early days of the new Republican administration, if not before, and with peace will come also a conclusion to the existing measures protecting the industry from foreign competition.

Unless action is taken during the session of Congress beginning in December, the dye bill will lose its parliamentary status and even if immediately reintroduced in the next Congress will have to go through the legislative mill, to the House Committee on Ways and Means, thence to the House; from there to the Senate Finance Committee and back again to the Senate where it is at present. Congress will be under pressure to expedite many important measures involving the whole country immediately it convenes in the extra session which it is expected will be called by President-elect Harding when he assumes the chair of the Chief Executive of the nation. There will be many measures which their supporters will urge as more important to the entire nation than the dye bill, and the latter measure may go over until revision of the tariff law is taken up. In that event delay in enactment of legislation protecting the industry will certainly be more than a few months.

Opponents of the dye bill have not very materially changed their position since the end of the last session of Congress. Senator Moses of New Hampshire, who recently returned to Washington, declared his position unchanged. He personally was not opposed to action on the dye bill at the short session of Congress, provided it was amended along the lines provided for in his amendments. He is still opposed to the dye bill as it was reported from the Finance Committee and will continue to fight against its enactment, he said. There existed among members of the Senate, he continued, a disposition to let the measure go over until general revision of the tariff law is undertaken by the next Congress.

There is no doubt but that Senator Moses is correct in saying that there exists such a disposition among members of the Senate, although how strong that disposition is and how many members are so inclined cannot be ascertained until a greater number of them return from their homes a few days before the convening of Congress in December. Those observers who have been inclined to doubt the possibility of passage of the dye bill as reported from the committee are inclined to the belief that the bill will go over for consideration by the next Congress. The attitude of Senators Penrose, Smoot, Lodge, and Watson will have an important bearing.

Senator Moses, continuing his vigorous fight against the measure, recently held a conference with Senator Lodge at the latter's home on his way to Washington, but did not obtain from the Massachusetts senator an expression of belief that action should be delayed.

Another factor in the situation which is not to be overlooked will be the attitude of Senator Harding. The President-elect will certainly have a great influence upon the course of the Senate. It is to be noted that Senator Frelinghuysen of New Jersey is one of the three members of the Senate who are accompanying Senator Harding on his vacation trip. The New Jersey senator is one of the most earnest supporters of the dye bill.

There seems little doubt but that efforts will be made to pass the measure through the Senate at the coming session, and also that there will be strong opposition from those senators who have already placed themselves in that position. So far as known here, the situation as to the numerical strength of the supporters is unchanged, and the question still is, whether or not those in charge of the measure can be persuaded of the importance of pressing it to a vote.

WOOD CHEMICAL INDUSTRY CONFERENCES

Commissioner Edward P. Costigan and C. R. DeLong, of the chemical staff of the Tariff Commission, will represent that body at conferences with representatives of the wood chemical industry which will be held at Detroit, Mich., on December 7, and at Buffalo, N. Y., on December 9. The conferences in both cities will be held in connection with a preliminary survey of the industry which has been prepared by the Commission, a tentative draft of which has already been sent to a limited number of manufacturers for criticism and suggestions.

In the letter of announcement to manufacturers it was stated that "the Commission now desires to hold a conference with representatives of the industry to discuss with them, somewhat informally, the competitive conditions in the industry and the advisability of further investigation before completing our report for Congress." Subjects which it is especially desired to discuss at the conferences include competition from Canadian products; domestic competition from fermentation acetone; relation of the export market to the industry in 1920; relation of prices of acetate of lime and methanol, in 1919 and 1920; and the effect of the cessation of war on the industry.

While the survey of the commission will be completed, of course, it is probable that it will not be published for public distribution unless Congress desires to have the information contained in it for its use in considering tariff action in connection with the industry. A bill providing for the levying of duties upon products of the industry was introduced in the House during last session but has not received consideration from the Ways and Means Committee.

Development in Canada of the process for the manufacture of acetic acid from calcium carbide to supply acetone, a solvent in the manufacture of cordite, which was perfected during the war, has led the Commission to the belief that some examination should be made as to the possible competition domestic manufacturers are to expect from this source.

The process for the production of acetone by fermenting corn will also be inquired into during the conference, to determine what effect the competition from this source will have upon the industry. This process was developed in the United States at Terre Haute, Ind., during the war.

Prior to the war the industry exported 40 per cent of its production of acetate of lime, exports amounting to 75,000,000 lbs. During the war the increased demand for munitions in this country brought about a decrease in exports, which reached a low point of 12,000,000 lbs., from which point they have climbed again until they amounted to approximately 30,000,000 lbs. in 1920.

While production figures are not available, these undoubtedly have climbed so that the exports for last year were not nearly the important portion of total production they were prior to the war. Munitions demands also brought about development of the wood chemical industry in other countries. This is so of Japan, which had none prior to the war. Outside of the United States, Austria-Hungary is the largest producing country in the world. All of these questions are linked up in the conditions affecting the domestic industry, since the end of hostilities. It is believed that adequate information can be obtained from the conferences with the manufacturers by the Commission to make unnecessary any further exhaustive investigation into the industry at the present time.

RESIGNATION OF DR. C. O. JOHNS

Dr. C. O. Johns, chief of the color and protein laboratories of the Bureau of Chemistry of the Department of Agriculture, has resigned to accept the offer made him by the Standard Oil Company of New Jersey, to be director of the research laboratory of the company. Dr. Johns has been connected with the Bureau for nearly six years. During the last year he has been in charge of the investigational plant of the Department on the experimental farm at Arlington, Va.

Dr. Johns delivered his farewell address at a meeting of the Washington chemists held last night at the Cosmos Club here, at which Dr. Atherton Seidell, vitamines expert of the United States Public Health Service, discussed "Chemistry of Vitamines" in the principal address of the meeting. Dr. William Blum, of the Bureau of Standards, was elected president of the society for the ensuing year beginning in January; J. B. Reed of the Bureau of Chemistry was reëlected secretary; and Dr.

F. B. Dewey, of the Bureau of the Mint, was named treasurer. Councilors elected were R. B. Sosman, W. D. Collins, F. W. Smither, W. M. Clark, and A. Seidell. The executive committee was composed of R. C. Wells, F. C. Cook, L. H. Adams, W. W. Skinner, F. F. Fitzgerald, and V. K. Chesnut.

Action is expected in the near future by Commissioner of Internal Revenue Williams on proposed restrictive regulations which have been prepared and submitted to him for approval, dealing with preparations of high alcoholic content which might be used for beverage purposes. In general it is proposed to restrict the sale of such preparations to stores of high reputation, eliminating the present practice of selling such goods to small retail stores which are not careful to see they are not used for beverage purposes by those who purchase them.

Experts of the Department of Agriculture will participate in the conference which is to be held December 6 and 7 in New York under the auspices of the Plant Protection Institute to discuss proper methods of using calcium arsenate and other poison dusts for the extermination of the boll weevil and other insects which damage crops. Use of calcium arsenate, it is said, is comparatively recent and there exists a need for education as to its proper use. Its efficacy, when used properly, is praised highly.

November 12, 1920

LONDON LETTER

By Stephen Miall, 28, Belsize Grove, Hampstead, N. W. 3, England

During the last month the British chemists have been more occupied in holidays than in anything else and there is but little news to chronicle.

Dr. Cottrell's paper on bringing chemists of all countries closer together, among other means by an auxiliary international language, gave me much opportunity for reflection. It is a question whether under changing conditions the Americans will be willing to spare the time to learn a new language which has no literature or individuality. In England it seems at the moment likely that there will in the near future be a considerable intercourse between us and our near neighbors, the French and the Belgians and I fancy a good many of us will spend our energies in improving our very poor French rather than in attempting to converse or write in Esperanto or some other more practical but less ornamental tongue.

A good deal has been published recently on atomic weights and the structure of the atom, but it has been a matter of some surprise here how slowly modern ideas have permeated into the minds of the industrial chemists. The work done by American chemists on atomic weights, particularly that of lead, originally attracted my attention to this subject and I have followed the recent work of Dr. Aston of Cambridge with the greatest of interest. It seems as if we are on the point of getting a real insight into the meaning of atomic weights, and that in a few months it will be definitely established that hydrogen atoms can combine to form helium and that these two will give rise to various combinations which will account for all the known chemical elements or compounds. A general letter of this character is not the place in which to attempt a detailed survey of the modern views on this subject, but such a survey is much needed; and many a chemist would read the story in a technical journal who has no time to read the purely scientific periodicals in which the information now gradually appears. Science has now become so specialized that only the amateur can glance at a number of branches. The expert on one subject usually has no time to keep in touch with other departments. I was reminded of this by your journal which I received while on my holiday. It contained a long account of the literature on the preserving of eggs, and I looked in vain in it for a reference to the work of Réamur. Perhaps the fact that he was a great naturalist and a competent physicist has made us forget some of his very varied researches. But if my memory is correct he made what was, in his day, a really scientific examination of the preserving of eggs.

September 12, 1920

....

FINANCIAL CONDITION

Every business man in Great Britain has a few problems to reflect upon in his leisure moments, and it should be borne in mind that most of us have less leisure than we had in the old pre-war days. Business at the present time is on the whole more difficult than it was and one has to work longer hours to carry it through; only the very few indeed make an attempt to be as well off as they were.

In pre-war times, which seem to us now to be almost as distant and ideal as the Golden Age, money was plentiful and most businesses could save an appreciable amount of their profits, partly investing these in foreign countries, and able to undertake developments and new extensions whenever these appeared to be profitable. Now there is no spare money for firms or the country as a whole; the money we send abroad is not an investment but is interest on debts we have contracted. Firms which could once comfortably embark on new processes and factories find that all their surplus goes in taxation. Money is not only very dear but also very hard to obtain. Banks have been obliged to arrange a sort of ration for loans to their customers, and at the same time prices remain very high and much more working capital is now needed for manufacturing the same number of tons of any product than was ever the case in the past. The bulk of the business men I come across are sufficiently occupied with these problems in their own concerns and have not much energy left or inclination for discussion of the great world problems in their spare time. If one asks for advice one gets the same suggestion everywhere, "Work hard, make as much money as you can, spend as little as possible, conserve your resources, live quietly, do not buy a new house or increase your style of living and try to impress on the Government the need for this and every other sort of economy." There is a general feeling that trade, which on the whole is not brisk now, will become worse in the winter, and certainly the feelings I have indicated above do not tend to an enterprising view of life or to a great demand on the part of consumers. The labor situation is difficult and interesting, but very few over here expect any serious trouble. Indeed many shrewd observers think that the relations between capital and labor here will, during the next ten or twenty years, be better than in America.

During the war the working men and women worked hard and earned very high wages and they were led to believe that never again would they have to endure the long hours, bad housing conditions, and limited opportunities of reasonable recreation and improvement of their lot which they had long put up with. Not only did their own leaders and the government of the day hold out these hopes, but there was, and still is, a genuine feeling among employers that labor is entitled to a better share in the good things of this world than formerly. The trouble is that we are now finding out how poor we are and how impossible it is at the present time to afford the gratification of any generous instincts which we may have. During the war we borrowed money freely and lived extravagantly and were glad to see the workers better fed, better clothed and better off, and we hoped so soon as the war was over to see them better housed. But the building of new houses is very expensive, probably unnecessarily so, and proceeds very slowly, and the workers are dissatisfied and suspicious. The majority of the men's leaders are well informed and realize the situation and do their best to keep the men to moderate courses, but naturally among a section of mankind the man who promises most is the most popular and by the time a labor politician becomes really experienced in political economy and fully informed on the problems from the point of view of both labor and capital he is suspected by the army he leads and has to make way for a man with less judgment and more prejudice.

COAL SITUATION

We have for weeks past been faced with a national coal strike, possibly supported by transport workers and others. It may take place; some of the miners' unions have large funds saved up for such a contingency and after all why not spend the money—posterity has done nothing for us. Mr. Smillie, the coal miners' leader, who was regarded two or three years ago as rather an extreme man, has now advised the miners against a strike and may for that reason lose a good deal of his hold over them. On this occasion public opinion is strongly against a strike and there is a belief that an increase of coal miners' wages has in the past usually been followed by a decline in production and that the same result may follow again. Some men in all grades of society dislike work, especially disagreeable work, and will not do more than suffices to provide for their accustomed needs. The policy of the English trades unions has rather tended to uniformity of production in the union and this really means coming down to the minimum, not raising up the unwilling to a maximum. I do not think this is the intention or the wish of the men's leaders; it is more due to their belief—unfounded in my opinion—that all men, in proper surroundings, will become more intelligent, more industrious, better educated, and with loftier ideals. They do not believe in helping a man to get out of his class and into a better one; their desire is to lift up the whole class together. The sort of class hatred which is spoken of in wild newspaper articles appeals, I believe, to a very small section indeed of the community. I do not imagine that nationalization of mines interests people here very much. It is an old idea and we have had a recent experience of state factories and government by men of business quite sufficient for this generation.

Nationalization of mines dates back to ancient Greece, and after the war between Athens and Sparta prices rose to about five times their pre-war level and one of the remedies proposed as a cure for unrest was the nationalization of the mines.

EXCESS PROFITS DUTY

A more exciting problem is that of the excess profits duty. This was supposed to be a tax during the war only. Every firm had a pre-war standard of profits and on the excess over that standard it paid 80 per cent to the government; for the year 1919 this was reduced to 40 per cent, which was increased this year to 60 per cent. The effect of this of course is to make it impossible for an enterprising and go-ahead firm to extend. The more it has developed since pre-war days the harder it is hit, and the balance of profits left after paying the duty does not in these days of high prices suffice to provide the additional working capital necessary for an increased output. Every manufacturer in the country wants to see the end of the excess profits duty and if this expired next spring would feel an immense relief. But the money has to be obtained somehow and no one is confident that this uneconomical and unfair tax will be abolished for another year or two. Meanwhile it does an immense amount of harm. Trade with other countries suffers from other uncertainties. Can anyone say whether the franc, the mark or the crown will be higher or lower three months hence? Some of the experts tell us that Germany still has recourse to the printing press in order to make both ends meet, relying on the old motto, "Let us be good and happy and live within our incomes even if we have to borrow money to do it." No one will be surprised if the mark gets worse before it gets better. In Belgium, which I visited in the early part of the summer, there appears to be already an extraordinary recovery, but this is a small country and more than half Europe is still in a state of paralysis.

October 12, 1920

PARIS LETTER

By Charles Lormand, 4 Avenue de l'Observatoire, Paris, France

PETROLEUM AND NATURAL GAS

The recent agreement between a syndicate of French manufacturers and bankers and the Standard Oil Company was extremely satisfactory from the industrial standpoint.

This question of petroleum is also of interest along another line. For the last two years engineers and geologists have done much prospecting on French soil, with a view of finding oil. M. Durandin has just published a complete atlas of the possible petroleum-bearing districts in France. At the same time M. P. Dolfus, one of the geologists best acquainted with the French subsoil, has made a study of the probability of finding oil. For theoretical reasons, he eliminates the regions of the north, west, southwest, and southeast; and the only region where he considers there is any chance of finding oil is in the neighborhood of the Saône valley, that is, Bresse and Bugey. The layers of this region should be a continuation of those of Pechelbronn. Several natural-gas wells have already been reported in that district.

There is still another line along which petroleum research is being conducted vigorously; that is, from the point of view that the natural gas may contain helium. This gas is also being sought in mineral waters. MM. Moureu and Lepape are resuming the examination of springs which they have already analyzed, as well as new springs, and are studying them both as regards helium and radioactivity.

M. Lepape has just reported, at Bagnères-de-Luchon, in the Pyrenees, a spring whose water contains 41.5 millimicrocuries of radium emanation per liter. Except for waters from the regions containing uranium ores, this is one of the highest contents ever found.

The separation of radium from barium by an easy fractionation has been studied by M. Denigès. Using iodic acid as a reagent, he has pointed out the difference in crystalline form of the iodates, and he believes that through their difference in solubility, he can secure a better separation than is now obtained.

NITROGEN FIXATION

As I have previously pointed out, the Claude process entering the realm of success. The initial installation produced o to 150 liters of ammonia per 24 hrs., and the "Badische niline" circulated the report that this amount, which was only large-scale laboratory experiment, could never be passed. . Claude denied this statement, declaring before the general eeting of the Société de l'Air Liquide that he has in operation an outfit producing a ton and a half of ammonia daily. Naturally he is going to try to increase his production still further.

The question of the catalyzer seems to be settled in favor of iron. M. Guichard has reached an analogous conclusion. During the war, MM. Urbain and Guichard, with other chemists, were requested by the government to study the nitrogen problem. They have just published a valuable report. After trying more than 500 substances as catalysts, they conclude that a ferro-molybdenum alloy gives the best yield.

FUELS

Although the mines in the north of France are being put into commission and the delivery of coal is becoming more regular, every possible economy in this line is being carefully considered.

The spread of a German process for the magnetic separation of cinders is announced. In this process it is claimed that 100 tons of coal produce 20 tons of ash, from which 5 tons of coke can be recovered by magnetic separation. These figures seem questionable, for the proportion of ash from coal is always less than here shown.

In France, separation is made by mechanical shaking and sifting, a process which gives very satisfactory results.

DIRECT OXIDATION OF ALCOHOLS

In the realm of organic chemistry MM. Moureu and Mignonac have just oxidized the alcohols directly, by passing a mixture of the alcohol vapor and oxygen over reduced silver as a catalyst. The corresponding aldehyde is obtained in excellent yields, almost theoretical for the lower alcohols, and of course decreasing slowly on going up in the series. They have thus succeeded in converting geraniol into citral.

In common with all the industries, the French chemical industry is passing through a crisis. The reaction from high salaries and the resultant high cost of living has brought about a decrease in buying. The stocks no longer sell and many industries are shutting down. The metallurgical and mechanical industries, where the drop in the price of coke has been felt from the beginning, were the first to be affected. The chemical industry is now beginning to feel the effect, and many factories are dismissing their employees, their stocks being too small to stand their production.

October 28, 1920

INDUSTRIAL NOTES

large paper mills are being completed at Niagara Falls y the Kimberly-Clark Company and the Paper Converting ompany. The Kimberly-Clark plant will be electrically perated. The company makes its own dyes and inks and manuctures its own electrotype plates.

A new Faculty of Applied Sciences and Technology is to be founded at Queen's University, Belfast, in association with the Belfast Municipal Technical Institute, to deal with such subjects as pure and applied physics, applied chemistry, bleaching and dyeing, textile industries, etc.

During the nine months ending September 30, 1920, exports of aniline dyes totaled nearly $17,000,000, while imports of all dyes totaled $4,277,131, a considerable increase over the same period in 1919. The colors not elsewhere specified, which include practically all the coal-tar colors except alizarin and indigo, were imported principally from Switzerland, Germany being in the second place. All the synthetic indigo imported in September came from France and all the alizarin from England. Exports during the same period showed an increase of over $5,000,000.

IMPORTS FOR NINE MONTHS ENDING SEPTEMBER 30

	1910	1920
Alizarin and alizarin dyes	$17,223	$151,917
Indigo, natural	162,566	138,251
Indigo, synthetic	219,353	435,766
Extracts for dyeing	122,145	152,927
Not elsewhere specified	2,185,055	3,398,270
TOTAL	$2,706,055	$4,277,131

At the Texas State Fair, which was held in October, was an exhibit by the Mexican government of the products of the Mexican republic. A prominent section of the display was occupied by drugs, chemicals, and by-products manufactured entirely in Mexico and on a scale which places the drug and chemical business among the foremost of Mexican industries. The largest drug and chemical manufacturing concern in Mexico is the firm of Francisco Paz y Puente, which included in its exhibit red iron oxide, malachite green, chrome yellow, mascot lime, whiting, etc. Although organized in 1870, almost the entire growth of this firm occurred after the outbreak of war in 1914. Cia Manufactuera de Pinturas y Barnias is a pioneer in the manufacture of chemicals, specializing in paints and colors. T. Bezanilla Cia specializes in medicinal specialties.

The soap industry of Belgium is rapidly returning to a normal basis, soft soap being manufactured in practically every important Belgian center. Hard household soaps are produced mainly at Brussels, Verviers, Antwerp and Mons, chiefly for domestic consumption. Although importations are still large, soap of home manufacture shows a tendency to replace the imported toilet soap. Soap powder for household and industrial use, medicinal soaps, and specialties are also manufactured in Belgium.

The Imperial Mineral Resources Bureau of England has issued four reports dealing with the production of arsenic during the war period in the Empire and foreign countries, with fuller's earth, with chrome ore, and magnesite. The production of arsenic in Canada has been increasing and now equals the production in England, while the output in the United States is in excess of the production of the whole British Empire. The United States increase has come not from new mineral sources but by the discovery of waste arsenic from smelter fumes and its transformation from a public danger to a valuable product. England was formerly the chief producer of fuller's earth, but the output fell from 31,000 tons in 1913 to 23,000 tons in 1918, while the output of the United States rose from 34,000 tons to 75,000 tons during the same period. Before the war Rhodesia and New Caledonia produced the bulk of the world's consumption of chrome ore. The output in Canada rose in 1917 to 33,000 tons, in India to 50,000 tons, and the United States to 83,000 tons.

A large addition to the chemical laboratory of the Elyria Enameled Products Company has just been completed, making it one of the best equipped industrial research laboratories along these lines. The new portion is devoted to the ceramic and chemical engineering departments, while the former structure is used as an analytical laboratory and contains the offices and library. The ceramic laboratory contains a complete experimental enameling plant, including smelters, mills, and furnaces. The chemical engineering laboratory contains a complete line of semi-commercial enameled units for the investigation of industrial problems, as well as metallographic equipment for research on problems arising from the heating of metals in the enameling processes. The laboratory is in charge of Mr. Emerson P. Poste, the ceramic engineering department in charge of Mr. B. A. Rice, and Mr. Max Donauer has charge of the chemical engineering laboratory.

At the first convention of the German chemists since 1914 held in Hanover during September, fuel was the principal problem discussed. The dye situation and the field of pharmaceutical drugs were also considered. Dr. Hans Goldschmidt of Berlin, speaking on "The Past and Future of the Chemical Industry," declared that in aniline dyes Germany was "beyond reproach," and that while Germany had lost the war, German science would not fail to restore German industries to the eminence previously held.

The United States Civil Service Commission has announced an examination for kelp plant assistant to fill a vacancy in the Bureau of Soils, Department of Agriculture, at Summerland, Cal., and positions requiring similar qualifications, at $1,800 to $2,400 a year. The duties will consist of the development of factory methods and supervision of the preparation of bleaching carbons from kelp charcoal, extraction of iodine from kelp brines, and superintendence of work connected with the extraction of potash from kelp. Competitors will be rated upon experience and reports covering investigations of kelp plant processes (to be filed with application). Applicants must have had at least one year's experience in connection with the handling of kelp plant processes, operating under the dry distillation method, and must have reached their twenty-fourth birthday. Applications must be filed with the Civil Service Commission, Washington, D. C., prior to the hour of closing business on December 7, 1920.

After conducting experiments for over three years, the Baltimore Pearl Hominy Company has announced the production of a new type of sugar, known as invertose, from corn. At the present time 25 bbls. are being produced daily, and additional machinery is to be installed to increase the daily production to 100 bbls. The invertose is made directly from whole corn, the process taking 6 hrs. Advantages over ordinary sugar substitutes are claimed, in that it is free from undesirable tastes and traces of undesirable chemicals. In dry form the invertose is 80 per cent as sweet as cane sugar, and in sirup form 65 per cent as sweet.

A few of the shareholders of Brunner, Mond & Co., Ltd., have brought suit to prevent the corporation from making the £100,000 gift to British universities for scientific education and research which was recently announced. It is understood that this suit is welcomed in order to test in advance the legality of this splendid contribution to research.

The Italian government is to resume its inquiry into the possibility of obtaining payable potash from the saline reserves of the Italian islands, in the hope of freeing Italy from dependence on foreign supplies.

Columbia University has announced a gift of $1,000 from the General Bakelite Co., to be used to maintain an industrial research fellowship in the chemical engineering department.

A fish fertilizer plant, financed by American capital, has been opened at Sauzal, Lower California, Mexico. The plant was erected by the territorial government in 1918 for converting kelp into material for powder. The war ended just as the plant was ready for operation, and the plant has been acquired by American capital and remodeled. It has a capacity of 150 tons of fish daily, and will produce fish-meal fertilizer with fish oil as a by-product. Later it is intended to install a cannery to pack the edible fish.

Manufacture of fertilizer on a small scale has been started at the Morris Fertilizer Works, at Navassa, N. C., whose $1,000,000 plant is nearing completion.

The Toronto Refining and Manufacturing Company and the Mona Oil Company are being organized in Canada with a combined capital of $5,000,000 for the manufacture of gasoline, using crude oil from Kentucky, Oklahoma, and Canadian oil fields. An option has been secured on the patent process for the manufacture of a special type of gasoline discovered by Dr. Trotter, of Alabama, which is claimed to produce a better oil than any on the market. The refinery will have a capacity of 10,000 bbls. daily.

The National Research Corporation has given $5,000 to Harvard University for research work on the manufacture of oxygen from the engineer's point of view. The investigation is now under way at the Harvard Engineering School, under the direction of Dr. H. N. Davis, professor of mechanical engineering.

The Bureau of Labor Statistics of the Department of Labor has just issued a bulletin containing a summary of the wages and hours of labor in various industries. Under the heading of the chemical industry the survey included establishments engaged in the manufacture of general chemicals, explosives, pigments, fertilizers, food products, petroleum products, soap, and sugar, for the period September 25, 1918, to May 31, 1919, no including any part-time pay rolls. During the period of t survey the activity of the industry in general was diminishi and because of cancellation of war contracts the contracti some branches was quite rapid.

The Gordon Dryer Corporation, which has for more t year been operated in affiliation with Grinnel Co., of Provi R. I., has started construction of a large plant in Warren, Ohio.

PERSONAL NOTES

Dr. Julius Stieglitz, of the University of Chicago, has delivered three lectures on the Mayo Foundation at Rochester, Minnesota. The first was on "Chemistry and Medicine," and the other two were on "The Electrical Theory of Oxidation."

The body of **Mr. Irwin J. Smith**, of Menands, Albany, N. Y., who died in Lens, France, as the result of injuries received in an automobile accident which occurred August 2, is being brought home to America. Mr Smith was a member of the American Chemical Society and widely known in business circles as being related to the textile and dyestuff trades throughout New York, Massachusetts, and Ohio. He was vice president and director of the Color Service Corporation, formerly Kalle Color & Chemical Co., of New York City, and vice president of the Surpass Chemical Co., of Albany, N. Y.

Mr. Charles E. Acker died recently at his home in Ossining, N.Y., after a long illness. Mr. Acker was a manufacturer and inventor, and was born at Bourbon, Ind., in 1868. He developed the first electrolytic process for the manufacture of caustic soda by the electrolysis of molten salt, known as the Acker process. The Elliott-Cresson gold medal of the Franklin Institute of Philadelphia and several other medals were conferred upon Mr. Acker for his invention. Mr. Acker was a director of the American Electrochemical Society and a member of the American & Chemical Society and other scientific organizations.

Mr. Charles F. Lindsay has been appointed technical assistant to the president of the U. S. Rubber Co., New York City.

Mr. Paul Poetschke has resigned as vice president and director of the department of chemistry of the Pease Laboratories, Inc., of New York City, and has again associated himself with the L. D. Caulk Co., Milford, Del., as director of the department of chemistry. Mr. Poetschke has been associated with the L. D. Caulk Company for the past eight years, and will now devote himself exclusively to research and development work for that company, including the supervision of manufacture of dental products.

Dr. G. H. Woollett, of the chemical faculty of the University of Minnesota, has been elected associate professor of chemistry at the University of Mississippi, University, Miss., with which university he was formerly connected for a short time; and **Dr. Victor A. Coulter**, who served as a gas officer in France, has been elected assistant professor of chemistry in the same institution.

According to a recent announcement, **Dr. Thomas H. Norton**, dye and chemical expert and a member of the American Chemical Society, has been appointed technical editor of the *Chemical, Color and Oil Daily.*

Dr. G. A. Burrell has resigned as president of the Island Refining Corporation to take charge of refinery construction for the France-Canada Shipping Corp., New York City. Dr. Burrell sailed for England on October 23 to be gone three months, in the interests of the latter company.

Dr. F. M. Perkin, son of Sir William Henry Perkin, discoverer of aniline, recently received the honor of the Order of Commander of the British Empire from the King of England. Dr. Perkin is one of the leading authorities upon the scientific treatment and utilization of coal and the production of oil from it.

According to a recent announcement the following have been elected officers of the American Pharmaceutical Association: President, **Samuel L. Hilton**, Washington, D. C.; First Vice President, **Charles E. Caspari**, St. Louis, Mo.; Second Vice President, **David F. Jones**, Watertown, S. D.; Third Vice President, **Hugo H. Schaefer**, New York; Members of the Council, **Henry M. Whelpley**, St. Louis, Mo.; **George M. Beringer**, Camden, N. J.; **John G. Godding**, Boston, Mass.

Dr. John B. Tuttle has severed his connection with the Firestone Tire & Rubber Co., as chief chemist of Plant 2, and has opened an office in New York City as a consulting chemist and rubber technologist.

Dr. Ellwood B. Spear, who recently joined the technical staff of the Goodyear Tire & Rubber Co., Akron, Ohio, has been appointed acting head of the research laboratory.

Mr. J. O. Lewis, chief petroleum technologist of the Bureau of Mines, has tendered his resignation and will be succeeded by **Mr. A. W. Ambrose**, who has for some time occupied the position of superintendent of the Bureau of Mines Petroleum Experiment Station at Bartlesville, Okla.

Dr. L. H. Baekeland recently gave a talk to the members of the Chemists' Club on his personal experiences in South America.

Mr. Guy R. McDole, assistant soils chemist in the Minnesota Agricultural Experiment Station, St. Paul, Minn., has accepted a position as associate professor of agronomy and soil technologist at the University of Idaho, Moscow, Idaho.

Mr. H. C. Colson, Jr., formerly chemist with Sharp & Dohme, Baltimore, Md., is now in charge of the department of pharmacology in the laboratories of Hynson, Westcott & Dunning of the same city.

Mr. H. D. Ruhm, for many years connected with the phosphate business in Tennessee and for some time president of the Ruhm Phosphate Mining Co., has severed his previous connections and is now in business for himself in New York City.

Mr. O. R. Sweeney, formerly professor and head of the department of chemical engineering at the University of Cincinnati, now holds a similar appointment at the Iowa State College, Ames, Iowa.

Prof. Calixte F. Bousquet has resigned from the chair of analytical chemistry at the Polytechnic School of the University of Montreal, Canada, to become head chemist of the West End Chemical Co., at West End, Cal.

Mr. Lee Irvin Smith has accepted a position as instructor of organic chemistry on the staff of the University of Minnesota, Minneapolis, Minn., for the coming year, having previously held a similar position on the staff at Harvard University, Cambridge, Mass.

Mr. O. A. Hougen has resigned as research chemist with the Carborundum Company, Niagara Falls, N. Y., to accept the position of assistant professor in the department of chemical engineering at the University of Wisconsin, Madison, Wis.

Mr. C. A. Sandberg, formerly assistant in chemistry at the University of California, has accepted a position as chemist for the National Lead Co., Oakland, Cal.

Mr. Oscar R. Smith has resigned his position as chemist and engineer of tests for the B. R. & P. Railway, DuBois, Pa., to become chief chemist for the Electric Alloy Steel Co., Charleroi Works, Charleroi, Pa.

Dr. Ralph K. Strong has recently taken charge of the work in chemistry at Reed College, Portland, Oregon, where special attention will be given to the chemical industries of Oregon, many of which are located in the vicinity of Portland. Dr. Strong has had several years' experience in this field as head of the department of chemical engineering at Oregon State College, Corvallis, Oregon.

Mr. Albert Salathe, a recent graduate student in the University of Chicago, has been appointed professor of chemistry and head of the department at the Albany College of Pharmacy, Albany, N. Y., and will still continue as vice president of the Organic Products Corporation, Schenectady, N. Y.

Miss Jessie E. Minor resigned as chief chemist of the Hamersley Manufacturing Co., Garfield, N. J., to accept a position as head of the pulp and paper department of the Emerson Laboratory, Springfield, Mass.

Mr. Harold W. Browning, instructor in botany at the University of Wisconsin last year, has a similar appointment at Rhode Island State College, Kingston, R. I.

Mr. C. E. Farrand, who assisted in chemistry at the State University of Iowa during the past summer session, is now professor of physical chemistry at Wabash College, Crawfordsville, Ind.

Mr. D. L. Scoles has resigned as assistant professor of chemistry at the Iowa State College, Ames, Iowa, to accept a position as professor of chemistry and head of the department at Illinois Wesleyan University, Bloomington, Ill.

Mr. J. L. Sherrick, formerly research chemist in colloids with E. I. du Pont de Nemours & Co., Delta Laboratory, Arlington, N. J., has accepted a fellowship investigating soap and other toilet articles at the Mellon Institute of Industrial Research, Pittsburgh, Pa.

Mr. Alan P. Sullivan has left his position with the Carborundum Co., at Niagara Falls, N. Y., to take charge of the research laboratory of the Stackpole Carbon Co., at St. Marys, Pa.

Mr. Walter Laib has tendered his resignation to the Ohio Salt Co., of Rittman, Ohio, where he was employed for over nine years as chief chemist and general superintendent, and will assume the position of treasurer and sales manager of the Cleveland Match Co., of Cleveland, O.

GOVERNMENT PUBLICATIONS

By Nellie A. Parkinson, Bureau of Chemistry, Washington, D. C.

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

DEPARTMENT OF LABOR

Industrial Survey in Selected Industries in the United States. 1919. Preliminary Report. Prepared under the supervision of A. H. Willett, Professor of Economics, Carnegie Institute of Technology, Pittsburgh, Pa. Labor Bureau Bulletin **265**. 509 pp. Paper, 75 cents. Covers general tables, arranged alphabetically.

GEOLOGICAL SURVEY

Abrasive Materials in 1918. F. J. Katz. Separate from Mineral Resources of the United States, 1918, Part II. 17 pp. Published August 27, 1920. This report is concerned with only those mineral products which are used for grinding and polishing and other abrasive operations and as cleansers or detersives. Statistics of production, both as to quantity and value, are given. Artificial abrasives are included for comparison and because of their strong influence on the industry and markets of natural abrasives. There was a slight increase in the total value of the abrasive materials included in this report as compared with 1917. This increase was in domestic natural abrasives and in imports, which combined more than offset a decrease in artificial abrasives.

Structure and Oil and Gas Resources of the Osage Reservation, Oklahoma. M. I. Goldman. Bulletin 586-X. 6 pp. 1920.

Lead in 1917. General Report. C. E. Siebenthal. Separate from Mineral Resources of the United States, 1917, Part I. 17 pp. 1920. The output of refined lead in the United States from domestic ores in 1917 was 548,450 short tons, valued at $94,333,000—a loss in quantity of 3,778 tons, or nearly 1 per cent, and a gain in value of $18,126,000, or nearly 24 per cent, as compared with 1916. The following table gives summary statistics of lead in the United States, 1912–1917, in short tons:

Surface Water Supply of the United States, 1917. Part XII. North Pacific Slope Drainage Basins. (C)—Lower Columbia River Basin and Pacific Slope Drainage Basins in Oregon. N. C. Grover, F. F. Henshaw and G. L. Parker. Prepared in coöperation with the states of Oregon and Washington. Water Supply Paper 464. 149 pp. Paper, 20 cents. 1920.

Surface Water Supply of the United States, 1918. Part II. South Atlantic Slope and Eastern Gulf of Mexico Basins. N. C. Grover, G. C. Stevens and C. G. Paulsen. Water Supply Paper 472. 56 pp. Paper, 10 cents. 1920.

Gypsum Deposits of the United States. R. W. Stone and Others. Bulletin 697. 326 pp. Paper, 50 cents. 1920. This bulletin was prepared to take the place of Bulletin 223 of the Geological Survey, "Gypsum Deposits in the United States," which was published in 1904. The report is divided into three parts: Part I, general discussion; Part II, gypsum deposits; Part III, bibliography. It includes 37 plate illustrations and 57 figures.

Mineral Resources of Alaska. Report of Progress of Investigations in 1918. G. C. Martin and Others. Bulletin 712. 204 pp. This volume is the fifteenth of a series of annual bulletins treating of the mining industry of Alaska and summarizing the results achieved during the year in the investigation of the mineral resources of the Territory. It contains an account of the mining industry, including statistics of mineral production, and also preliminary statements on investigations made by the Geological Survey.

Copper in 1918. General Report. B. S. Butler. Separate from Mineral Resources of the United States, 1918, Part I. 59 pp. Published September 28, 1920. The outstanding features of the copper industry for the year 1918 were the shortage and inefficiency of labor and the difficulties of transportation. The net result was that domestic production and imports showed little change from 1917. There was a notable increase in domestic consumption and an equally notable decrease in exports.

Peat in 1919. K. W. Cottrell. Separate from Mineral Resources of the United States, 1919, Part II. 6 pp. Published October 14, 1920. There was a decided decrease in both the quantity and value of domestic peat marketed in 1919. This decrease may doubtless be attributed to the high cost of labor and the lack of transportation facilities. The total production of peat in the United States in 1919 was 69,197 short tons, valued at $705,532, an average price per ton of $10.20. This was a decrease of 35 per cent in quantity and of 33 per cent in value, but an increase of 44 cents in the price per ton, compared with 1918.

	1912	1913	1914	1915	1916	1917
Total production of refined primary lead[1] in the United States	480,894	462,460	542,122	550,055	571,134	610,769
Production of desilverized lead in the United States	339,646	330,593	383,903	388,594	403,619	422,266
Production of soft lead in the United States (including desilverized soft)	171,037	161,300	201,725	205,462	235,759	244,771
Production of antimonial lead in the United States	13,552	16,665	16,667	23,224	24,038	18,646
Production of lead from domestic ores	392,517	411,878	512,794	507,026	552,228	548,450
Production of secondary lead in the United States	67,168	72,834	61,062	78,900	96,300	93,500
Consumption of primary lead in the United States (disregarding stocks)	394,113	414,283	451,264	430,252	461,238	517,685

[1] "Primary lead," which is produced directly from ore, is here distinguished from "secondary lead," which is obtained by refining skimmings, drosses' and old metals. Wherever in this report the word "lead" is used without qualification it means primary lead.

Surface Water Supply of the United States, 1917. Part I. North Atlantic Slope Drainage Basins. N. C. Grover, C. H. Pierce, C. C. Covert and G. C. Stevens. Prepared in coöperation with the states of Maine, Vermont, Massachusetts, and New York. Water Supply Paper 451. 163 pp. 1920.

Surface Water Supply of the United States, 1917. Part XI. Pacific Slope Basins in California. N. C. Grover, H. D. McGlashan and F. F. Henshaw. Prepared in coöperation with the state of California. Water Supply Paper 461. 314 pp. Paper, 25 cents. 1920.

Stone in 1918. G. F. Loughlin and A. T. Coons. Separate from Mineral Resources of the United States, 1918, Part II, 125 pp. Published October 11, 1920. The year 1918 was a most disastrous one for the stone industry in general. The total quantity sold in 1918 was about 68,563,360 short tons, a decrease of about 18 per cent from the quantity in 1917, which was, in turn, a decrease of about 9 per cent from that in 1916. No stone showed an increase in total quantity sold in 1918, although the sales for a few uses increased in quantity. The following table shows the value of the different kinds of stone sold in the United States from 1908 to 1918:

YEAR	Granite	Basalt and Related Rocks (Trap Rock)[1]	Sandstone	Marble	Limestone	Miscellaneous[2]	Total
1908	$18,420,080	$4,282,406	$7,594,091	$7,733,920	$27,682,002	....	$65,712,499
1909	19,581,597	5,133,842	8,010,454	6,548,905	32,070,401	....	71,345,199
1910	20,541,967	6,452,141	7,930,019	6,992,779	34,603,678	....	76,520,584
1911	21,194,228	6,739,141	7,730,868	7,546,718	33,897,612	....	77,108,567
1912	19,223,302	7,560,049	6,893,611	7,786,458	36,729,800	....	78,193,220
1913	20,733,217	9,134,494	7,248,965	7,870,890	38,745,429	....	83,732,995
1914	20,160,730	7,865,998	7,501,808	8,121,412	33,894,155	....	77,544,103
1915	17,864,439	8,489,222	6,095,800	6,916,025	35,229,866	....	74,595,352
1916	17,456,838	7,666,297	5,603,778	7,033,171	41,309,599	....	79,069,683
1917	15,544,957	7,570,885	5,512,421	6,330,387	46,263,379	$993,642	82,215,671
1918	14,466,423	7,782,280	4,529,298	5,496,389	49,453,006	973,034	82,700,430
Percentage of increase or decrease in 1918	−6.9	+2.8	−17.8	−13.2	+6.9	−2.1	+0.59
Percentage of total	17.5	9.4	5.5	6.6	59.8	1.2	....

[1] The term "trap rock" has been variously interpreted and in some localities has been made to include a number of widely different rocks. It is here replaced by the title "basalt and related rocks."

[2] Includes mica schist used for furnace lining, conglomerate, argillite, and various light volcanic rocks used mainly for crushed stone, which can not be properly classified in any of the main groups.

Because of the process of general reconstruction in which the mineral industries are involved, a brief historical review of the stone industry is given.

PUBLIC HEALTH SERVICE

A Study of the Dust Hazard in the Wet and Dry Grinding Shops of an Ax Factory. C. E.-A. WINSLOW AND LEONARD GREENBURG. Public Health Reports, 35, 2393–2401.

Some Phases of Protein Catabolism and Fatigue. E. L. SCOTT AND A. B. HASTINGS. Public Health Reports, 35, 2445–62.

Outbreak of Gastroenteritis and Typhoid Fever Caused by Pollution of Public Water Supply at Schenectady, N. Y. THEODORE HORTON. Public Health Reports, 35, 2549–56.

Ultraviolet Rays in Water Purification. Some Abstracts from the Literature on the Sterilization of Water by Use of Ultraviolet Rays. Reprint No. 576 from Public Health Reports. 6 pp. Paper, 5 cents.

Efficiency of Certain Devices for Protection of Sand Blasters against Dust Hazard. C. E.-A. WINSLOW, LEONARD GREENBURG AND E. H. REEVES. Reprint No. 585 from Public Health Reports. 18 pp. Paper, 5 cents.

Ozone in Ventilation. Some Abstracts from the Literature on the Use of Ozone in Ventilation. Reprint No. 591 from Public Health Reports. 7 pp. Paper, 5 cents.

BUREAU OF MINES

Monthly Statement of Coal-Mine Fatalities in the United States, July 1920. W. S. ADAMS. 8 pp. Paper, 5 cents. 1920.

Bibliography of Petroleum and Allied Substances, 1917. E. H. BURROUGHS. Bulletin 180. Petroleum Technology 54. 170 pp. Paper, 25 cents. 1920.

The Manufacture of Sulfuric Acid in the United States. A. E. WELLS AND D. E. FOGG. Bulletin 184. 216 pp. Paper, 40 cents. 1920. The bulletin covers the main facts in regard to the sulfuric acid industry in this country, including a discussion of the supplies of sulfur-bearing raw materials, the situation of the acid plants, the principal points in regard to manufacturing processes, and the uses of the acid. Most of the data were obtained directly from observation and from coöperating acid companies or from individuals who had been or are now engaged in acid manufacturing.

Production of Explosives in the United States during the Calendar Year 1919 with Notes on Coal-Mine Accidents Due to Explosives, and List of Permissible Explosives Tested May 31, 1920. W. W. ADAMS. Technical Paper 259. 31 pp. Paper, 5 cents. 1920. The total production (excluding exports) of explosives in the United States during the year ended December 31, 1919, was 417,634,470 lbs., as compared with 499,124,660 lbs. in 1918, a decrease of 81,490,190 lbs. or 16 per cent. The decrease in the output of explosives was due almost entirely to the fact that the coal and metal mining industries during 1919 used 84,700,000 lbs. of explosives less than in 1918.

Coke-Oven Accidents in the United States during the Calendar Year 1919. W. W. ADAMS. Technical Paper 266. 25 pp. Paper, 5 cents. 1920. A gratifying decrease is shown in the number of men killed in 1919, as compared with the previous calendar year. The number of men killed in 1919 was 53 and in 1918 it was 73, while the number injured was 4,031 in 1919 and 7,792 in 1918. The total number of men reported employed in 1919 was 28,741; during the previous year it was 32,389.

BUREAU OF STANDARDS

Standard Samples Used or in Preparation. Supplement to Circular No. 25. 6 pp. 1920. This circular replaces and supersedes the supplement issued February 28, 1920, as well as all previous supplements. In tabular form is given a descriptive list of standard samples, with schedule of weights and fees and averaged analyses of irons, steels, alloy steels, sheet brass, argillaceous limestone, zinc ore, manganese ore, Lake Superior iron ores, magnetite iron ore, and pure chemicals, including sugars, naphthalene, benzoic acid and sodium oxalate. Ordering and shipping regulations are also included.

Recommended Specification for Liquid Paint Drier. Circular 105. Prepared and recommended by the U. S. Interdepartmental Committee on Paint Specification Standardization, September 27, 1920. 4 pp. Paper, 5 cents. Issued October 18, 1920. This specification applies both to straight oil drier (material free from resins or "gums") and to Japan drier (material containing varnish "gums"). General specifications are outlined, as well as methods of sampling, laboratory methods, and the basis of purchase.

Enamels for Sheet Iron and Steel. Technologic Paper 165. J. B. SHAW. 88 pp. Paper, 15 cents. 1920. The report includes an introduction, a description of the properties and preparation of steel for enameling, raw materials for enamels, preparation of enamels, enameling process, calculation of enamel formulas, physical properties of enamels, and resistance of enamels to chemical action.

Laboratory Wearing Test to Determine the Relative Wear Resistance of Sole Leather at Different Depths throughout the Thickness of a Hide. R. S. HART. Technologic Paper 166. 7 pp. Paper, 5 cents. The results are obtained from a series of preliminary tests. From the data obtained, the interior portions of the leather appear to have a greater resistance to wear than either the grain or flesh sides. There is no specific surface which has the greatest wear resistance.

DEPARTMENT OF AGRICULTURE

American Sumac: A Valuable Tanning Material and Dyestuff. F. P. VEITCH, J. S. ROGERS AND R. W. FREY. Department Bulletin 706. Issued July 26, 1918; Revised November 6, 1920. 13 pp. Paper, 5 cents.

Manufacturing and Laboratory Tests to Produce an Improved Cotton Airplane Fabric. FRED TAYLOR AND D. E. EARLE. Department Bulletin 882. 48 pp. Paper, 10 cents. Issued October 9, 1920.

Turpentine: Its Sources, Properties, Uses, Transportation and Marketing, with Recommended Specifications. F. P. Veitch and V. E. Grotlisch. Department Bulletin 898. 51 pp. Paper, 15 cents. Issued November 8, 1920.

The Production and Utilization of Corn Oil in the United States. A. F. Sievers. Department Bulletin 904. 23 pp. Issued October 29, 1920.

Sugar-Cane Juice Clarification for Sirup Manufacture. J. K. Dale and C. S. Hudson. Department Bulletin 921. 15 pp. November 1920.

Drug Plants under Cultivation. W. W. Stockberger. Farmers' Bulletin 663. 50 pp. Paper, 10 cents. Revised 1920.

Waterproofing and Mildewproofing of Cotton Duck. H. P. Holman, B. S. Levine and T. D. Jarrell. Farmers' Bulletin 1157. 13 pp. October 1920.

COMMERCE REPORTS—OCTOBER 1920

An order has been issued by the government at Auckland, Australia, prohibiting the exportation of **kauri** which has been adulterated with any other gum. (P. 14)

The maximum of the **paper** scarcity in Australia has not yet been reached and there is no likelihood of relief for a year. (P. 14)

The Canadian **paint** and **varnish** industry is reviewed. (Pp. 18–21)

Statistics are given showing the imports and exports of **vegetable oil** and vegetable oil material by Italy during 1917, 1918, and 1919. (Pp. 22–3)

Dyes and dyestuffs exported from the United States in August 1920 amounted to $2,111,095, of which $1,151,196 represented aniline dyes and $336,718 logwood extract. China was by far the largest importer. Statistics are given showing the value of the exports according to countries. (P. 25)

It is reported that drastic steps are contemplated by the Rubber Growers' Association in order to raise the price of raw **rubber**. (P. 30)

Laundry soap is now being manufactured in numerous places in the Dutch East Indies, so that the demand for imported soap is limited. (P. 30)

There are innumerable small oil mills in southern India for the manufacture of **peanut oil** and the possibilities for trade development in this line are good. (P. 37)

Uruguay is considering the establishment of a factory for the manufacture of **superphosphates** for use as fertilizers. (P. 47)

Recent developments in the recovery and utilization of waste slate in England have led to the extension of processes for the production of paints, distempers, putty, brick, blocks, slabs, tiles, mortar, plaster, flooring, rubber, and molded goods. (P. 53)

A million dollars' worth of German **dyes** were imported into Japan during August. (P. 56)

A factory, equipped with the most modern apparatus for the production of **sulfuric acid** in large quantities, has been installed recently in Montevideo. The capacity of the plant is greater than the needs of the country. (P. 63)

The resumption of work in the Belgian **chemical industry** was 74 per cent in December 1919 as compared with 95 per cent in June 1920. (P. 69)

The **iron** and **steel** industry of South Africa is reviewed. (Pp. 72–3)

There is a demand in Sweden for **soda sulfate**. (P. 78)

The **mineral** resources of the Swatow District in China are considerable, including coal, iron, wolframite, bismuth, tin, manganese, lead, silver, molybdenite, and pyrites. (P. 82)

Statistics are given showing the imports and exports of vegetable oil and vegetable oil material by China during 1917, 1918, and 1919. (P. 86)

The United States foreign trade for 1919 and 1920 in finished coal-tar colors and **indigo** is reviewed. (Pp. 87–91)

Chinese crops are reported to be suffering for lack of **chemical** elements. (P. 116)

A decree has been issued in Belgium modifying the price of **alcohol**. (P. 158)

New Zealand's trade in **fertilizers** is reviewed. (Pp. 164–5)

The world's **copper** production is reviewed. The following table shows the world's production of copper for every fifth year from 1803 to 1918:

Year	Metric Tons	Year	Metric Tons	Year	Metric Tons
1803.........	15,000	1843.......	42,000	1883.....	199,000
1808.........	16,000	1848.......	52,000	1888.....	262,285
1813.........	17,000	1853.......	63,000	1893.....	310,704
1818.........	19,000	1858.......	78,000	1898.....	441,868
1823.........	23,000	1863.......	96,000	1903.....	609,985
1828.........	27,000	1868.......	110,000	1908.....	790,238
1833.........	31,000	1873.......	122,000	1913.....	1,002,300
1838.........	36,000	1878.......	154,000	1918.....	1,395,160

(Pp. 171–5)

Attention is called to the large deposits of **iron ore** and **limestone** in Finnish Lapland. (Pp. 194–5)

The use of **insecticides** and **fungicides** in South Africa is reviewed. (Pp. 199–202)

The **zinc industry** in pre-war Russia from 1863 to 1914, inclusive, is described. (Pp. 204–7)

The republic of Colombia is looked upon as a promising field for the exploitation of **petroleum** resources. These resources and the laws pertaining thereto are described. (Pp. 226–36)

Statistics are given showing that the increase in the production of Chilean **nitrate of soda** for the first 8 mo. of 1920 over the production for the same period in 1919 was 10,801,169 quintals, and that the increase in the exportation was 33,382,411 quintals. The trade is now on the basis of normal supply and demand. (Pp. 236–7)

Experimental work is being conducted by the Queensland Agricultural Department on an extensive scale in the cultivation of the **castor oil** plant. These beans have been found to contain from 46 to 52 per cent of oil. (P. 238)

The glass trade of Canada, of which the United States is the chief supplier, is reviewed. (Pp. 249–51)

Nearly a mile of new bore has been sunk during the present year in drilling for **oil** in the United Kingdom. In only one case has a well proved productive. (P. 266)

Gum arabic is now available for shipment from Argentina. (P. 275)

Regulations issued by the United States Post Office regarding the packing of dyes, in powder form, for dispatch to foreign countries, are quoted. (P. 277)

The **mineral resources** of the Amazonian region of Bolivia are restricted to the petroleum deposits, some iron ores, and deposits of gold. (P. 292)

The use of **compressed gas** in foreign countries is described. (P. 311)

Iron ore deposits have been discovered in Switzerland which, at pre-war consumption rate, will be sufficient, it is estimated, to meet domestic needs for 45 years. (P. 313)

By an ordinance passed by the Gold Coast Colony Legislative Council on May 25, 1920, the importation of certain specified **dyestuffs** is prohibited. (P. 323)

The Spanish **paper** situation is reviewed. (P. 327)

There has been a great increase in the exports of **paper, pulp,** and cellulose from Finland this year. (Pp. 328–9)

Some particulars relative to the new degumming method for **ramie fiber**, which has been the subject of study and experimentation by British experts for some years, are described. (Pp. 330–1)

The extraordinary depression existing in the usually lively **rubber** market of Amsterdam is due to low prices and the consequent indisposition of sellers to accept offers. The low prices are attributed to reduced demand, especially in the United States. (P. 337)

The possibilities and prospects of developing a **wood pulp** industry in the southern part of Chile, where the islands and mainland are thickly forested, are reviewed. (Pp. 350–1)

A change in the regulations governing the denaturing of **alcohol** for industrial purposes has been made by the Canadian government, with view to making industrial alcohol available to the arts and sciences at a more reasonable price than at present. (P. 352)

The **rubber industry** of Bolivia, one of the most important industries in Bolivia, is reviewed. (Pp. 373–81)

Much interest is being displayed in the report of rich deposits of **silver** and **lead ore** at Baratata Station, South Australia. (P. 394)

The estimated production of **starch** in the Kokkaido, Japan, for 1920 is from 116,000,000 to 132,000,000 lbs., compared with 178,573,950 lbs. in 1919. (P. 403)

The **petroleum** situation in Rumania is reviewed. (Pp. 406–8)

In addition to natalite, there has recently been produced in South Africa another motor fuel, known as **"acetol."** The basis of this new fuel is alcohol and ether which comprises 90 per cent. It is said that this new fuel apparently solves the question of the air-cooled engine. (P. 411)

Attention is called to the **mineral** resources of Bulgaria, and it is stated that the valuable mineral wealth of Bulgaria has never been known and now needs only exploiting. (P. 423)

It is estimated that there are in the **peat** fields near La Paz, Bolivia, 150,000,000 cubic meters of peat, which would yield 30,000,000 tons of dried peat briquets. (Pp. 424–5)

It is estimated that the region north of Bogota contains enough **salt** to supply Colombia for centuries. (P. 435)

The New Zealand government is still assisting private interests in prospecting for **petroleum** within the Dominion. (P. 443)

The **arsenic** industry in Japan is reviewed. In 1918, 1,828,198 lbs. of arsenic ore valued at $9,204, were produced. The output increased to 2,133,281 lbs. in 1919, but its value decreased to $6,975. (Pp. 444–5)

Mineral production in Spain is reviewed. It is conservatively estimated that the output of copper pyrites in Spain represented about 60 per cent of the world's production in 1918, and the Spanish mines are now in position to produce more than before the war. (Pp. 446–7)

A new Italian process for the manufacture of synthetic **ammonia** is described. (Pp. 452–3)

The transport of American **mineral oil** supplies to Austria during the past few months has succeeded beyond all expectation and it is believed that the Austrian demand for lighting oil has been covered for the next few months. (P. 466)

Leather is being produced from rabbit skins in Australia by a secret process. (P. 476)

The production and industrial uses of **sesame seed** in Mexico is reviewed. (Pp. 486–7)

The **lizard-skin** industry forms a new branch in the hides and skins trade in India. (P. 490)

SPECIAL SUPPLEMENTS ISSUED IN OCTOBER

DENMARK—5*a*
NETHERLANDS—11*a*
SPAIN—18*b*
UNITED KINGDOM—22*g*
DUTCH GUIANA—47*a*

STATISTICS OF EXPORTS TO THE UNITED STATES

CANADA—(P. 447)
- Paper
- Pulp

LIVERPOOL (P. 255)
- Ferromanganese
- Palm oil
- Fertilizer other than bone meal
- Bone-meal fertilizer
- Tungsten

LONDON—(P. 312)
- Rubber
- Hides
- Leather
- Tin
- Drugs and chemicals
- Gum
- Lead
- Copper
- Creosote oil
- Aluminium
- Scrap metal
- Linseed oil

NETHERLANDS—(P.68)
- Crude rubber
- Linseed oil
- Gelatin

BOOK REVIEWS

Animal Fats and Oils. By Louis Edgar Andés. 3rd English Edition, translated from the German and revised and enlarged by H. B. Stocks. viii + 315 pp. 76 illustrations. Scott, Greenwood and Son, 8 Broadway, Ludgate Hill, E. C. 4, London, 1920. Price 15s, net.

The reviser in his preface states that he has endeavored to blend practical experience with scientific knowledge and has extended the scope of this volume by adding new material, as well as thoroughly revising the old subject matter to bring it strictly up to date, and that he hopes he has succeeded in producing a useful companion as a textbook to "Vegetable Fats and Oils" and "Drying Oils."

The reviewer, however, does not feel that this has been accomplished, at least when viewed from American practice, although this book may measure up very well with European standards. It is another case in which the Americans have outstripped the Europeans in labor-saving devices; because the apparatus and methods set forth in this volume can in no sense be considered up-to-date or in keeping with the best practices now employed in the fat industries of this country.

The volume contains a great many typographical errors and transpositions. It is also lacking in bibliography, and it would appear to the writer that a great deal of the descriptive matter could have been omitted and covered by references or bibliography. The reviser has failed to give references to the original literature in his quotations from other authorities. The methods of analysis are entirely inadequate as they stand, without the proper references to the original literature. In fact, the reviser has failed entirely to grasp the importance of the personal equation in analytical work; and has failed to give proper attention to the matter of detailed manipulation, so important in analytical methods, especially where used for commercial purposes.

The first chapter treats in a brief way of the nature, origin, and preparation of animal fats, together with the progress made in methods of producing and recovering them.

In Chapter II the author deals with the constitution of animal fats. In giving methods of saponification, however, he makes no mention of the sufo-acids or castor-bean pulp, although the former play such an important role in the American fat industry. In his enumeration of alcohols he fails to make any mention of trimethyleneglycol which has also become quite a troublesome factor in the fat and glycerol industry. As above stated, this chapter contains a great many mistakes in the writing of chemical formulas, as well as transpositions of physical and chemical constants. Lanolin is described as almost pure cholesterol, while in a later chapter it is more correctly classified as hydrated wool grease containing 11 per cent cholesterol or isocholesterol. The amount of space devoted to the discussion of shark-liver oil is entirely out of proportion to its value among the animal fats.

Chapter III is devoted to the preparation of animal fats and oils from their crude sources. Here again entirely too much detail is employed, and a great many processes and forms of apparatus are described which American manufacturers would consider obsolete.

Edible animal fats, including butter, lard, and tallow, are treated in the first part of Chapter IV, while the balance of the chapter is devoted to fats used in industrial processes. Among and included in this category are bone fats, neat's foot oil, horse fats, and bone oil. Garbage grease and tankage extraction grease which would properly come under this chapter have been entirely overlooked, and no mention is made of them here or in Chapter VII, which deals with waste or recovered animal fats.

Chapter V deals with fish and sea-animal oils, and appears to be concise and to cover the subject fairly well. Chapter VI is devoted to miscellaneous oils, under which the author classifies egg oil, turtle oil, candle-fish oil, alligator oil, hare oil, goose oil, and human fat. It would be interesting to know how many if any of the data given on human fat were derived from experiments conducted on the battle fields of Europe. Chapter VII is devoted to waste and recovered greases, and a greater part of the chapter is given over to a discussion of sophisticated "Degras," while tankage and garbage greases which are of greater importance to the fat industry are entirely overlooked.

Chapter VIII gives a fairly good chronology of the hydrogenation processes. Chapter IX is devoted to physical and chemical examinations of oils and fats, and from an educational or a technical viewpoint it is absolutely worthless as it stands, because the methods are so abbreviated and lacking in detail of manipulation as to be absolutely worthless for practical application.

ARCHIBALD CAMPBELL

Chemistry for Textile Students. By BARKER NORTH AND NORMAN BLAND. viii + 379 pp. Cambridge University Press, Cambridge, England, or G. P. Putnam's Sons, New York, 1920. Price, $9.00.

This book is novel in that it emphasizes the important chemicals and the processes in which they are used in the textile industry. Divided into four parts and an appendix, under which tables of vapor pressure of water, hygrometry, hydrometry, strength and specific gravities of common acids and alkalies are given, it is designed for the student who is pursuing chemistry in conjunction with studies in yarn manufacturing and other allied subjects of the industry. It would be useful in the instruction of the average evening student who wishes to obtain a general knowledge of the application of chemistry. It can serve as a reference for chemists who are not directly in textile work. It is rather simple in its explanations, written so as to be understandable and adaptable to those of limited prior education. It is not thorough enough for those students making a specialty of the study of the chemistry of the industry and dyeing.

In scope, the book is wide. The first part is devoted to the fundamental principles of chemistry, omitting the study of the metals. The authors depend a great deal on the suggested experiments to make clear their point. These experiments are admirably chosen, but a large number are too complicated and involved in apparatus for student use and must necessarily be carried out by the instructor.

The material is well chosen and is about what is generally accepted as the most important for the man who will be connected in general mill capacity, but not specializing in chemistry. As an illustration, a conception of valency is given instead of a clear scientific discussion, and this method of simplicity of presentation is used throughout the book.

Parts of the work are too heavy for the elementary student. An example of this is the volumetric determination of acids and alkalies which, while thorough in explanation, can lead only to rule-of-thumb methods because of lack of preparation. This point is given, no doubt, because of the vast importance of acids and alkalies in the various scouring and dyeing operations.

Much stress is laid upon water, its softening, and methods for testing hardness. Under atmosphere, the moisture and carbon dioxide content are studied in relation to (1) amount of moisture in textile fibers and the effect on the various spinning operations, and (2) the effect of carbon dioxide in relation to improper ventilation of textile mills. Under carbon, considerable space is devoted to gaseous fuels and their estimation; the Orsat apparatus is also shown, and methods given for analysis of furnace gas.

Part 3 is devoted to the chemistry of the hydrocarbons and those derivatives which are principally used in textile work. Under hydrocarbons, petroleum and methods for its physical testing are introduced. They are studied from two angles, *i. e.*, the lubrication of machinery and the oiling of wool fibers during manufacture. Under ether is shown the Soxhlet apparatus and its use in removing grease from material. Under aldehydes the compound with sulfoxylate used in stripping of dyes and discharge work is emphasized. Under fatty acids, formic, acetic and the higher fatty acids of soap manufacture are considered. The chapter on dibasic acids deals mostly with oxalic, tartaric, and citric acids. Under carbohydrates, starch and its modifications, and cellulose are brought forward. The chapter on benzene derivatives is brief and deals mostly with coal tar and tannins. All these products are widely used in textile work.

A chapter is devoted to a brief study of textile fibers. Also some considerations are given to the bleaching, mordanting, and mercerizing processes.

Altogether this book can be thoroughly recommended as the only one of its kind, and the authors are to be congratulated in the presentation of this work, and especially in the manner in which their one hundred illustrations add to the value of the book. The title of the book has been correctly chosen.

ELMER C. BERTOLET

Modern Pulp and Paper Making. By G. S. WITHAM, SR., Manager of Mills, Union Bag and Paper Corporation, Hudson Falls, N. Y. 599 pp. The Chemical Catalog Company, Inc., New York, 1920. Price, $6.00.

It cannot be said of the pulp and paper industry that there is any embarrassment of choice as regards textbooks. Until the appearance of the volume under review, students of papermaking had to depend on reprints of works dealing with machinery and manufacturing processes that pertained to an era in which precision of methods was not the universal rule.

The arrangement of Mr. Witham's volume is unusual, but it is questionable whether the value of the work would be enhanced by a change. It starts with a summary of the process by which pulp is produced, followed by a brief consideration of the materials of pulp and their preparation. Then comes a chapter on "The Varieties of Paper," which includes notes and observations on the substances which enter into their composition. These three chapters bring the reader to page 53. After this we go to the beginning of things and make the acquaintance of the saw mill where the logs of wood are treated preliminary to conversion into pulp. The equipment of the saw mill is described in great detail, beginning with the varieties of chains or log haul-ups employed to transport the wood from the water to the slashers or swing saws which may be used to cut the logs into pieces of the requisite size, usually 24 in., for subsequent conveyance to the wood room.

After a description of the wood room with its equipment of barkers, chippers, and chip screens, a profusely illustrated chapter of 23 pages, the reader is taken through the sulfite mill and acid plant, the various types of apparatus being described and illustrated in a way that is calculated to appeal in a very special manner to the practical papermaker. Although the author evidently presupposes a good working knowledge of apparatus and processes on the part of the student, it should not be difficult for the beginner or the non-technical reader to visualize his descriptions, and gain a correct idea of the technic of sulfite engineering work. An example of the author's minuteness of detail is shown in his discussion of sulfite digesters where he tells how the lining of a digester is constructed so as to avoid the contact of liquor with the steel shell.

The soda process for the manufacture of chemical wood pulp is described with a wealth of detail in a chapter occupying 29 pages, two-thirds of the space being given up to recovery methods, or the means by which the soda employed in cooking the fibers is afterwards regained from the spent liquor, by evaporating to a given consistency and then incinerating it, whereby the organic matter is oxidized, and the alkali remains, to be afterwards leached from the black ash and recausticized. The apparatus employed in the cycle is fully illustrated and competently described. In this chapter the author has drawn freely on the work of committees of the Technical Association of the Pulp and Paper Industry, thus assuring a thoroughly modern and scientific presentation of the subject. Praise must be accorded for the ingenious and interesting manner in which Mr. Witham has woven into a connected narrative a number of papers and reports from different sources.

The chapter on the sulfate process is a disappointing one, being given a rather cursory treatment. From the outline sketch of the procedure of cooking wood to obtain kraft pulp, which the author dignifies throughout with a capital initial, one gets no intimate detail of working conditions. As in the soda process, the recovery system gets the bulk of attention.

Space is not available to review, dissect, or expound the remaining chapters of Mr. Witham's interesting volume. Being a practical papermaker he devotes a large part of his work to the design, equipment, and operation of the machine room where the paper is formed. This comes after a description of the beater room where the pulps are mixed and combined with the necessary loading materials and sizing and coloring. Inserted in the chapter on the machine room is a pen and ink diagram showing, on one side, the progress of materials through a typical pulp mill from the river and saw mill to the beater room, and on the other a sectional view of a Fourdrinier machine, from the screens and wire at the wet end through the presses and dryers to the calender stack at the dry end. The subsequent chapters on the general design of pulp, paper, and power plants, the handling of employees, and the testing of paper serve the purpose of assembling, in convenient form for reference, a vast amount of material that is scattered throughout numerous engineering and paper technology journals. In the chapter on paper-testing methods no attempt has been made to give analytical methods, either microscopical or chemical. This is a defect in the book which might well be remedied in a subsequent edition by the insertion of a special monograph prepared by some person who has specialized in this branch of paper technology.

Witham's "Modern Pulp and Paper Making" will be heartily welcomed by all engaged in the practical work of manufacturing pulp or paper, as the need for such a volume has long been felt by mill superintendents and engineers, as well as by mill architects and constructors. Although the author has refrained from treating historical developments or the chemical aspects of processes at any length, the particulars he gives and the references which he quotes are adequate for a volume of the scope of this one, which is more especially intended for practical readers.

THOMAS J. KEENAN

The Yeasts. By ALEXANDRE GUILLIERMOND, Professor of Botany, University of Lyon. Translated and revised by FRED WILBUR TANNER, University of Illinois. xviii + 434 pp., 6 x 9. 163 figures. John Wiley & Sons, Inc., New York City, 1920. Price, cloth, $6.00. Chapman and Hall, Ltd., London, England. Price, 33s. net.

This English edition is based on Guilliermond's "Les Levures," which was published in 1912 in the Encyclopedie Scientifique. It is not, however, a mere translation of the previous French publication. The subject has developed so rapidly since 1912 that the translator with the collaboration of the author has added much new material.

Commenting on the reason for this publication the author sums up as follows:

> It seemed useful to me to collect into one book all of the knowledge required on the morphology, physiology, and taxonomy of this group of fungi, and to arrange it in such a manner that the data would be available for biologists, practitioners in industrial work, agriculturalists, and physicians.

That he has succeeded is indicated by the table of contents. The book comprises thirteen chapters.

Chapter I deals with the morphology and development of the yeasts, including a discussion of their forms, methods of propagation, sexuality, and germination; while Chapter II discusses the cytology, giving especial attention to the nucleus, cytoplasm and cell membrane, as well as the changes taking place in the cell during fermentation, multiplication, and sporulation.

Chapters III and IV, which have been revised and rewritten by the translator, deal with the physiology, nutrition and respiration of the yeasts, and also with alcoholic fermentation. It is in these chapters that one gets the first real knowledge of the multitude of chemical reactions taking place within this little cell. It is shown to be an intricate chemical laboratory, as it were, where all the reactions which we are wont to consider in the human system, such as digestion, assimilation, respiration, oxidation, and reduction, are taking place. The following enzymes have been shown to be present:

> (1) *Proteases:* zymase or alcoholase; endotryptase; a casease; a doubtful proteoclastic enzyme, acting like pepsin; an antiprotease; and an enzyme similar to rennin.
>
> (2) *Nucleases:* guanase; arginase; lipase; an amidase; and a deamidase.
>
> (3) *Carbohydrate enzymes:* glycogenase, amylase and inulase; raffinase, melibiase, and melezitase; sucrase, maltase, lactase, and trehalase; and an emulsion which splits methyl glucosides into methyl alcohol and glucose.
>
> (4) *Oxidizing and reducing enzymes:* catalases, and philothion or "hydrogenase;" and oxidases.
>
> (5) *Toxins:* an endotoxin capable of killing the yeast when extracted from the cell and introduced into culture media.

Fermentation is discussed through 23 pages. Here it is shown that the formation of alcohol is merely correlated with anerobic development, and is more active when oxygen is absent. In the presence of oxygen the yeast functions like a plant, but when placed in a reduced air supply it gives up or suppresses almost completely its multiplication. Alcoholic fermentation then becomes the source from which the plant draws its energy; the scarcer the oxygen, the slower the multiplication.

These two chapters by Dr. Tanner are very well written, and show much painstaking effort. There is, however, an unfortunate typographical error in the script on page 62 under "Polysaccharides," line 20. Here the word "maltose" is used when the enzyme maltase is referred to. The corrected reading should be—"This is transformed by *maltase* into glycose, etc." In Chapter IV, Dr. Tanner has made brief mention of the presence in yeast of the so-called vitamines which are the accessory substances vital to our newer knowledge of nutrition, and has quoted the important papers dealing with these essential elements, as they are found in yeasts.

Chapters V to VII discuss the origin, and the methods of culture, isolation, and identification of the yeasts. Chapter VIII discusses the variation of species, and Chapters IX and X deal with their classification into saccharomycetes and non-saccharomycetes. The last three chapters of the book deal with the doubtful yeasts, pathogenic yeasts, and the related fungi.

The work has a very complete list of footnote references which will be of great assistance to those wishing to consult the original authorities. It is, for the most part, notably free from typographical errors, is printed on good paper, and is easily readable. It contains a bibliographical index, as well as an author and a subject index.

The book should prove invaluable to biologists and industrial workers who are concerned with purely fermentation products, as well as agriculturists. Fifteen pages in Chapter XII deal with the pathogenic yeasts. For the industrial chemist who is interested in the chemical composition of these various species from the standpoint of the analysis of the ash, with especial reference to the quantity of phosphorus present, and the variation in the amounts of nitrogenous and fatty matter, it is hoped that a subsequent volume will supply this omission. The book should find a place on the shelves of every up-to-date library.

Howard T. Graber

The Making, Shaping, and Treating of Steel. By J. M. Camp and C. B. Francis. xxxviii + 614 pp. Carnegie Steel Co., Pittsburgh, Pa., 1920. Price, $5.00.

This book, published by the Bureau of Instruction of the Carnegie Steel Co., covers the entire metallurgy of steel, including the by-product coke oven and its products, pig iron, Bessemer, open-hearth and electric steel making, and heat treating. It was written especially for the non-technical employees of the Carnegie Steel Co., and others seeking a general knowledge of the metallurgy of iron and steel.

It is divided into three parts of 10, 11, and 4 chapters, respectively, each chapter being subdivided into numerous sections.

The introductory chapter deals with the general principles of physics and chemistry, and is well done. Exception must be taken to the definition of an alloy on page 8, and the table on page 11, which needs to be revised. The melting temperature of tungsten, for instance, is recorded as 1700° C., whereas it is 3400° C. Mention is made of the electronic constitution of matter, but none is made of the periodic relations of elements.

The chapter on refractories contains many useful data. It, however, is a handbook in nature, leaving out entirely the equilibria curves which so well explain the properties on refractories.

The chapter on fuels is unusually well written, the thermochemistry being surprisingly complete for so general a book. Under the head of pyrometers no mention is made of errors to be avoided in pyrometry. In the classification of fuels water gas has been left out of the list of gaseous fuels. The description of the by-product coke plant and its products is very clear and complete for a book of this nature.

The chapters dealing with the manufacture of pig iron, and the Bessemer, open-hearth and electric-furnace manufacture of steel, and the duplex and triplex process are all excellent, both in descriptive matter and in the discussion of the chemistry involved. In all cases, however, more illustrations are needed.

Part II, on the shaping of steel, contains chapters on the mechanical properties of steel, mechanical treatment of steel, the rolling mill construction and operation, preparation of the steel for rolling, including ingot defects, the rolling of blooms and slabs, the rolling of billets and semifinished products, including a discussion of their defects, the rolling of heavy finished products and large sections, the rolling of merchant mill products, circular shapes, and the forging of axles, shafts and round shapes. These chapters have condensed into 215 pages an unusually clear and helpful description of rolling-mill practice. It is especially good in the discussion of roll designs. In the reviewer's opinion more attention should have been given to the evil results of permitting ingots to cool too much between the teeming platform and the soaking pits, and the evils resulting from steel carelessly handled in the last hour of its stay in the open-hearth furnace.

Part III, on the constitution, heat treatment, and composition of steel, commences with a chapter on "steel as an alloy of iron and carbon," describing the constituents of steel and discussing the general theory of freezing of alloys. On page 521 the authors are in error in their statement concerning the percentage composition of the crystals of freezing gold-silver alloys, and again on page 525 the same error is made concerning the composition of freezing iron-carbon crystals. The chapter, however, is very clearly written, considering its necessary brevity.

The remaining chapters, dealing with annealing, hardening, tempering, toughening, and case hardening; the influence of the elements in steel on its mechanical properties, and alloy steels, are more readable than those of any text in common use.

To summarize, this book is the best general text on the market covering in a reasonably detailed way the metallurgy of cast iron and steel, including the subject of coke and fuels. It does not, of course, touch upon malleable cast iron and wrought iron. The book's chief weakness is its lack of illustrations.

D. J. Demorest

A Metallographic Study on Tungsten Steels. By Axel Hultgren. viii + 95 pp. John Wiley and Sons, Inc., New York, 1920. Price, $3.00.

The book is essentially a reprint of a thesis for the doctor's degree, to which the author has added an appendix dealing with the work of other investigators of the same alloys. The experimental work was carried out with carbon-tungsten steels, and the results are grouped in two sections. Part I deals with the transformations which occur when tungsten steels of varying composition are annealed and subsequently cooled at rates varying from sudden quenching to slow furnace cooling. The structural changes occurring under varying conditions are described in detail and illustrated by many excellent photomicrographs. Part II describes the author's experiments in attempting to determine the formulas of the carbides existing in the tungsten-carbon steels, and includes the results of the direct carburizing of tungsten steels and the effects of welding various carbon steels with tungsten. The resulting products were studied in part by the microscope and in part by the method of separating the different carbides by solvents. From this data the author has constructed tentative equilibrium diagrams of the system Fe–W–C. A long appendix contains a detailed review of the work of Honda and Murakami on the same subject.

The book contains much experimental work of great value. It is unfortunate that the author could not have presented the information in a more readable form. The difficulty is due in part to the nature of the work, much of which consisted in the repetition of experiments differing from each other only in the composition of the material used and variations in cooling conditions, and in part to the fact that the book is a translation from the Swedish. It is also to be regretted that one who is evidently very familiar with the properties and behavior of tungsten steels should have devoted so little space to their industrial applications and should have said nothing about the high-speed tool steels containing tungsten.

The book is well printed, on excellent paper, and contains 75 photomicrographs, most of which are of a high quality and clearly reproduced.

R. S. Williams

NEW PUBLICATIONS

American Lubricants. Lockhart. 2nd ed., revised. 341 pp. Price, $4.00. The Chemical Publishing Co., Easton, Pa.

Bibliography of Investigations Bearing on the Composition and Nutritive Value of Corn and Corn Products. M. Helen Keith. 178 pp. Price, $2.00. Research Information Service, National Research Council, Washington, D. C.

Catalysis and Its Industrial Applications. E. Joblino. 2nd ed. 144 pp. 12 illustrations. Price, $2.25. P. Blakiston's Son & Co., Philadelphia.

Chemical French. Dolt. 2nd ed., revised. 413 pp. Price, $4.00. The Chemical Publishing Co., Easton, Pa.

Chemical Research: Notes on Chemical Research. W. P. Dreaper. 2nd ed. 195 pp. Price, $2.50. P. Blakiston's Son & Co., Philadelphia.

Drying: Théorie et Pratique du Séchage Industriel. Paul Razous. 256 pp. Illustrated. Price, 25 fr. Dunod, Paris.

Dyestuffs: Application of Dyestuffs, to Textiles, Paper, Leather and Other Materials. J. Merritt Matthews. 768 pp. 292 figs. Price, $10.00. John Wiley & Sons, Inc., New York.

Explosives: Dictionary of Explosives. Arthur Marshall. 159 pp Price, $3.75. P. Blakiston's Son & Co., Philadelphia.

Food Industries. Vulte-Vanderbilt. 3rd ed., revised and enlarged. 325 pp. 82 illustrations. Price, $3.00. The Chemical Publishing Co., Easton, Pa.

Gas Warfare. Edward S. Farrow. 253 pp. Price, $3.00. E. P. Dutton & Co., New York.

Iron: Électrométallurgie du Fer et de ses Alliages. Jean Escard. 811 pp. Illustrated. Price, 90 fr. Dunod, Paris.

Metallurgy: Le Chauffage Industriel. Henry Le Chatelier. 536 pp. Illustrated. Price, 36 fr. Dunod, Paris.

Mineralogy: An Introduction to the Study of Minerals and Crystals. Edward H. Kraus and Walter F. Hunt. 560 pp. 696 illustrations. Price, $4.50. McGraw-Hill Book Co., Inc., New York.

Mineral Industry. Vol. 28, 1919. Edited by G. A. Roush and Allison Butts. 941 pp. Illustrated. Price, $10.00. McGraw-Hill Book Co., Inc., New York.

Mineral Resources: Political and Commercial Geology and the World's Mineral Resources. Edited by J. E. Spurr. 561 pp. 22 illustrations. Price, $5.00. McGraw-Hill Book Co., Inc., New York.

Nitrogen Fixation: Production Industrielle Synthétique des Composés Nitrés et leurs Dérivés. Jean Escard. 260 pp. Illustrated. Price, 30 fr. Dunod, Paris.

Organic Chemistry: A Laboratory Manual of Organic Chemistry for Medical Students. Matthew Steel. 2nd ed., revised and enlarged. 284 pp. Price, $1.75. John Wiley & Sons, Inc., New York.

Organic Chemistry: A Textbook of Organic Chemistry. E. de Barry Barnett. 380 pp. 15 illustrations. Price, $5.00. P. Blakiston's Son & Co., Philadelphia.

Organic Chemistry: A Textbook of Organic Chemistry. A. F. Holleman. 5th English ed., completely revised. 642 pp. 88 figs. Price, $3 50 net. John Wiley & Sons, Inc., New York.

Petroleum: Handbook of Petroleum, Asphalt, and Natural Gas. Roy Cross. 500 pp. Price, $5.00 net Bulletin No 15 of Kansas City Testing Laboratory, Kansas City, Mo.

Pumping by Compressed Air. Edmund M. Ivens. 2nd ed., revised and enlarged. 266 pp 124 figs. Price, $4.00 net. John Wiley & Sons, Inc., New York.

Qualitative Analysis: A Course of Instruction in the Qualitative Chemical Analysis of Inorganic Substances. Arthur A. Noyes. 8th ed., entirely rewritten. 182 pp. Price, $2.25. The Macmillan Co., New York.

Qualitative Analysis: Notes on Qualitative Analysis. Mason. 8th ed., revised. 58 pp. Price, $1.00. The Chemical Publishing Co., Easton, Pa.

Rubber: Technologie du Caoutchouc Souple. R. de Fleury. 210 pp. Illustrated. Price, 18 fr. Dunod, Paris.

Science and Life. Frederick Soddy. (Aberdeen Addresses.) 229 pp. Price, $4.00. E. P. Dutton & Co., New York.

Steel: Rapid Methods for the Chemical Analysis of Special Steels, Steel-Making Alloys and Graphite. Charles Morris Johnson. 3rd ed. 540 pp. Price, $5.00. John Wiley & Sons. Inc., New York.

Sugar: The Manufacture of Sugar from the Cane and Beet. T. H. P. Heriot. (Monographs on Industrial Chemistry.) 462 pp. Price, $8 50 net. Longmans, Green & Co., New York.

NEW JOURNALS

Brennstoff-Chemie: Zeitschrift fur Chemie und Chemische Technologie der Brennstoffe und ihrer Nebenprodukte. Editor, Dr. Franz Fischer, Kaiser-Wilhelm Institut, Mülheim. Published semimonthly by W. Girardet, Essen, Germany. Price, single copy, 2.50 M.; quarterly, including foreign postage, 18 M.

Ecology. Official journal of the Ecological Society of America. A continuation of *Plant World.* Editor, Major Barrington Moore. Published quarterly. Managed through Brooklyn Botanic Garden, Brooklyn, N. Y.

Physikalische Berichte. Replacing *Fortschritte der Physik, Halbomonatliches Literaturverzeichnis der Fortschritte der Physik,* and *Beiblätter zu den Annalen der Physik.* Published semimonthly by Deutsche Physikalische Gesellschaft and Deutsche Gesellschaft für Technische Physik, Braunschweig, Germany.

RECENT JOURNAL ARTICLES

Antiseptics: Stability of Chloramine Antiseptics. Jules Bebie. *Journal of the American Pharmaceutical Association*, Vol. 9 (1920), No. 10, pp. 974–979.

Brass: Melting Brass with Fuel Oil. S. D. Rickard. *The Metal Industry*, Vol. 18 (1920), No. 10, pp. 460–463.

Brass: Reclamation of Metal from Brass-Foundry Refuse. F. L. Wolf and G. E. Alderson. *The Metal Industry*, Vol. 18 (1920), No. 10, pp. 452–455.

Cellulose: The Preparation and Properties of a Highly Oxidized Cellulose. Edmund Knecht and Leonard Thompson. *Journal of the Society of Dyers and Colourists*, Vol. 36 (1920), No. 10, pp. 251–255.

Coal: Temperatures at Which Ash from Western Coals Fuses to a Sphere. W. A. Selvig, L. R. Lenhart and A. C. Fieldner. *Coal Age*, Vol. 18 (1920), No. 14, pp. 677–682; No. 17, pp. 851–854.

Cost Records of Production in Chemical Manufacture. E. W. McCullough. *Chemical Age*, Vol 28 (1920), No 10, pp. 365–366.

Dyeing of Paper. O. Kress. *Color Trade Journal*, Vol. 7 (1920), No. 5, pp. 160–163.

Essential Oils: Some Constituents of Essential Oils and Their Structural Relations. Ingo W. D. Hackh. *Journal of the American Pharmaceutical Association*, Vol. 9 (1920), No. 10, pp. 948–958.

Fertilizer: Plant Food Elements. R. N. Brackett. *The American Fertilizer*, Vol. 53 (1920), No. 9, pp. *72c*–*72e*.

Fertilizer: Sulfur as a Fertilizer. Charles A. Shull. *Science*, N. S., Vol. 52 (1920), No. 1347, pp. 376–378.

Filters: Design of Mechanical Filters. Balfour Bramwell. *The Chemical Age* (London), Vol. 3 (1920), No. 71, pp. 442–443.

Fuels: Impurities of the Air We Breathe and Their Relation to Fuel Economy. John B. C. Kershaw. *Combustion*, Vol. 3 (1920), No. 4, pp. 27–31.

Fuels: Modern Development of Fuel Gasification. Hubert Hermanns. *The Blast Furnace and Steel Plant*, Vol. 8 (1920), No. 11, pp. 617–624.

Fuels: Powdered Fuel for Chemical Plants. H. D. Savage. *Combustion* Vol. 3 (1920), No. 4, pp 32–33.

Hydrogen: The Structures of the Hydrogen Molecule and the Hydrogen Ion. Irving Langmuir. *Science*, N. S., Vol. 52 (1920), No. 1349, pp. 433–437.

Iron: Electric Furnaces and the Sulfur Problem in Cast Iron. George K. Elliott. *The Iron Age*, Vol. 106 (1920), No. 15, pp. 919–920.

Iron: Experiments on the Corrosion of Iron and Steel. William D. Richardson. *Canadian Chemical Journal*, Vol. 4 (1920), No. 10, pp. 275–279.

Lead Plating from Sodium Hydroxide Lead Baths by the Use of Addition Agents. F C. Mathers. *The Metal Industry*, Vol. 18 (1920), No. 10, pp. 467–468.

Leather: Il "Metodo a Scuotimento, Modificato" nell'Analisi delle Sostanze Concianti. G. Baldracco and S. Camilla. *Giornale di Chimica Industriale ed Applicata*, Vol. 2 (1920), No. 9, pp. 499–504.

Leather: On the Swelling and Falling of White Hide in Vegetable Tan Liquors. George D. McLaughlin and Ralph E. Porter. *Journal of the American Leather Chemists' Association*, Vol. 15 (1920), No. 10, pp. 557–581.

Leather: Some Considerations on the Testing of Dyes in the Leather Industry. Louis Joseph Matos. *Journal of the American Leather Chemists' Association*, Vol. 15 (1920), No. 10, pp. 553–557.

Lime: Manufacture of Lime for Chemical and Metallurgical Purposes. I. Richard K. Moore. *Chemical and Metallurgical Engineering*, Vol 23 (1920), No. 17, pp. 841–844.

Metallurgy: Dosamento dell'Arsenico e del Fosforo nei Materiali Siderurgici Comuni. Ignazio Compagno. *Giornale di Chimica Industriale ed Applicata*, Vol. 2 (1920), No. 9, pp. 493–497.

Methanol: A New Method for the Estimation of Methyl Alcohol. S. B. Schryver and Cyril C. Wood. *American Journal of Pharmacy*, Vol. 92 (1920), No. 10, pp. 720–728

Mineralogy: The Nomenclature and Classification of Sulfide Minerals. Edgar T. Wherry. *Journal of the Washington Academy of Sciences*, Vol. 10 (1920), No. 17, pp. 487–496.

Open-Hearth Process: The Basic Open-Hearth Process. F. L. Toy. *The Iron Age*, Vol. 106 (1920), No. 18, pp. 1116–1118; No. 19, pp. 1193–1195.

Refractometer: The Use of the Refractometer in Ascertaining the Purity of Certain Refined Edible Oils. F. H. Trim. *Journal of the Society of Chemical Industry*, Vol. 39 (1920), No. 18, pp. 307*t*–308*t*.

MARKET REPORT—NOVEMBER, 1920

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

		Nov. 1	Nov. 15
Acid, Boric, cryst., bbls	lb.	.15	.15
Hydrochloric, com'l, 22°	lb.	.02	.01⅞
Hydriodic	oz.	.19	.19
Nitric, 42°	lb.	.07¾	.07¾
Phosphoric, 50% tech	lb.	.25	.25
Sulfuric, C. P.	lb.	.07	.07
Chamber, 66°	ton	21.00	20.50
Oleum 20%	ton	23.00	23.00
Alum, ammonia, lump	lb.	.04¾	.04¾
Aluminium Sulfate (iron-free)	lb.	.04½	.04½
Ammonium Carbonate, pwd	lb.	.16	.16
Ammonium Chloride, gran	lb.	.12½	.12½
Ammonia Water, carboys, 26°	lb.	.11	.11
Arsenic, white	lb.	.13½	.13
Barium Chloride	ton	100.00	90.00
Nitrate	lb.	.14	.14
Barytes, white	ton	30.00	30.00
Bleaching Powd., 35%, Works	100 lbs.	6.00	5.00
Borax, cryst., bbls	lb.	.09	.09
Bromine, tech	lb.	.55	.55
Calcium Chloride, fused	ton	33.50	33.50
Chalk, precipitated, light	lb.	.05	.05
China Clay, imported	ton	18.00	18.00
Copper Sulfate	100 lbs.	7.25	7.25
Feldspar	ton	8.00	8.00
Fuller's Earth	100 lbs.	1.00	1.00
Iodine, resublimed	lb.	4.35	4.00
Lead Acetate, white crystals	lb.	.13	.13
Nitrate	lb.	.15	.15
Red American	100 lbs.	.12¼	.12¼
White American	100 lbs.	.10½	.10½
Lime Acetate	100 lbs.	2.50	2.50
Lithium Carbonate	lb.	1.50	1.50
Magnesium Carbonate, Tech	lb.	.13	.13
Magnesite	ton	65.00	65.00
Mercury flask	75 lbs.	60.00	55.00
Phosphorus, yellow	lb.	.35	.35
Plaster of Paris	100 lbs.	1.50	1.50
Potassium Bichromate	lb.	.26	.23
Bromide, Cryst	lb.	.50	.40
Carbonate, calc., 80–85%	lb.	.18	.17
Chlorate, cryst	lb.	.18	.18
Hydroxide, 88–92%	lb.	.22	.18
Iodide, bulk	lb.	3.25	3.00
Nitrate	lb.	.12	.12
Permanganate, U. S. P.	lb.	.65	.60
Salt Cake	ton	Nominal	Nominal
Silver Nitrate	oz.	.55	.53
Soapstone, in bags	ton	12.00	12.00
Soda Ash, 58%, bags	100 lbs.	2.25	2.10
Caustic, 76%	100 lbs.	4.10	4.10
Sodium Acetate	lb.	.11	.11
Bicarbonate	100 lbs.	3.00	3.00
Bichromate	lb.	.10½	.08
Chlorate	lb.	.10	.10
Cyanide	lb.	.29	.24
Fluoride, technical	lb.	.20	.20
Hyposulfite, bbls	100 lbs.	4.00	4.00
Nitrate, 95%	100 lbs.	3.00	2.90
Silicate, 40°	lb.	.01½	.01½
Sulfide	lb.	.08½	.08½
Bisulfite, powdered	lb.	.07	.07
Strontium Nitrate	lb.	.15	.15
Sulfur, flowers	100 lbs.	4.00	4.00
Crude	long ton	20.00	20.00
Talc, American, white	ton	20.00	20.00
Tin Bichloride	lb.	.19½	.19½
Oxide	lb.	.50	.50
Zinc Chloride, U. S. P.	lb.	.50	.50
Oxide, bbls	lb.	.10	.10

ORGANIC CHEMICALS

		Nov. 1	Nov. 15
Acetanilide	lb.	.45	.35
Acid, Acetic, 28 p. c.	100 lbs.	3.75	3.75
Glacial	lb.	.11	.10½
Acetylsalicylic	lb.	.80	.75
Benzoic, U. S. P., ex-toluene	lb.	.75	.75
Carbolic, cryst., U. S. P., drs.	lb.	.15	.15
50- to 110-lb. tins	lb.	.23	.23
Citric, crystals, bbls	lb.	.58	.52
Acid (*Concluded*)			
Oxalic, cryst., bbls	lb.	.25	.20
Pyrogallic, resublimed	lb.	2.35	2.35
Salicylic, bulk, U. S. P.	lb.	.40	.35
Tartaric, crystals, U. S. P.	lb.	.54	.50
Trichloroacetic, U. S. P.	lb.	4.40	4.40
Acetone, drums	lb.	.16	.16
Alcohol, denatured, 190 proof	gal.	1.10	.85
Ethyl, 190 proof	gal.	5.50	5.50
Wood, Pure	gal.	2.80	2.30
Amyl Acetate	gal.	4.00	4.00
Camphor, Jap. refined	lb.	1.20	1.10
Carbon Bisulfide	lb.	.08	.08
Tetrachloride	lb.	.12	.12
Chloroform, U. S. P.	lb.	.40	.40
Creosote, U. S. P.	lb.	.65	.65
Cresol, U. S. P.	lb.	.18	.18
Dextrin, corn	lb.	.05	.04½
Imported Potato	lb.	.11	.10
Ether, U. S. P., conc., 100 lbs	lb.	.24	.24
Formaldehyde	lb.	.25	.18
Glycerol, dynamite, drums	lb.	.24	.20
Pyridine	gal.	2.75	2.75
Starch, corn	100 lbs.	3.93	3.43
Potato, Jap	lb.	.06½	.06½
Rice	lb.	.25	.25
Sago	lb.	.05	.05

OILS, WAXES, ETC.

		Nov. 1	Nov. 15
Beeswax, pure, white	lb.	.60	.55
Black Mineral Oil, 29 gravity	gal.	.22	.22
Castor Oil, No. 3	lb.	.14	.13
Ceresin, yellow	lb.	.13	.13
Corn Oil, crude	lb.	.08½	.08½
Cottonseed Oil, crude, f. o. b. mill	lb.	.07¾	.07¾
Menhaden Oil, crude (southern)	gal.	.45	.40
Neat's-foot Oil, 20°	gal.	1.65	1.65
Paraffin, 128–130 m. p., ref	lb.	.11½	.11½
Paraffin Oil, high viscosity	gal.	.45	.45
Rosin, "F" Grade, 280 lbs	bbl.	12.90	12.00
Rosin Oil, first run	gal.	.69	.69
Shellac, T. N.	lb.	.90	.85
Spermaceti, cake	lb.	.30	.30
Sperm Oil, bleached winter, 38°	gal.	1.85	1.85
Stearic Acid, double-pressed	lb.	.19½	.19½
Tallow Oil, acidless	gal.	1.25	1.25
Tar Oil, distilled	gal.	.60	.60
Turpentine, spirits of	gal.	1.26	1.09

METALS

		Nov. 1	Nov. 15
Aluminium, No. 1, ingots	lb.	.28	.28
Antimony, ordinary	100 lbs.	6.75	6.75
Bismuth	lb.	2.72	2.72
Copper, electrolytic	lb.	.14¾	.13
Lake	lb.	.15	.13¼
Lead, N. Y.	lb.	.06¾	.06½
Nickel, electrolytic	lb.	.45	.45
Platinum, refined, soft	oz.	90.00	90.00
Quicksilver, flask	75 lbs ea.	60.00	55.00
Silver	oz.	1.00	1.00
Tin	lb.	.40½	.37½
Tungsten Wolframite	per unit	6.50	6.50
Zinc, N. Y.	100 lbs.	7.00	6.80

FERTILIZER MATERIALS

		Nov. 1	Nov. 15
Ammonium Sulfate	100 lbs.	4.80	3.85
Blood, dried, f. o. b. N. Y.	unit	5.10	5.10
Bone, 3 and 50, ground, raw	ton	45.00	45.00
Calcium Cyanamide, unit of Ammonia		4.00	4.00
Fish Scrap, domestic, dried, f. o. b. works	unit	5.00	5.00
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%	ton	6.85	6.85
Tennessee, 78–80%	ton	11.00	11.00
Potassium Muriate, 80%	unit	2.25	2.10
Pyrites, furnace size, imported	unit	.18	.18
Tankage, high-grade, f. o. b. Chicago	unit	4.00	4.00

COAL-TAR CHEMICALS

Crudes

		Nov. 1	Nov. 15
Anthracene, 80-85%	lb.	.75	.75
Benzene, Pure	gal.	.35	.30
Cresol, U. S. P.	lb.	.18	.18
Cresylic Acid, 97-99%	gal.	1.20	1.20
Naphthalene, flake	lb.	.10½	.08
Phenol, drums	lb.	.13	.08
Toluene, Pure	gal.	.35	.35
Xylene, 2 deg. dist. range	gal.	.60	.60

Intermediates

		Nov. 1	Nov. 15
Acids:			
Anthranilic	lb.	2.20	2.20
B	lb.	2.25	2.25
Benzoic	lb.	.75	.75
Broenner's	lb.	1.75	1.75
Cleve's	lb.	2.00	2.00
Gamma	lb.	4.00	3.75
H	lb.	1.70	1.65
Metanilic	lb.	1.70	1.70
Monosulfonic F	lb.	3.50	3.50
Napthionic, crude	lb.	.85	.85
Nevile & Winther's	lb.	1.80	1.80
Phthalic	lb.	. 0	.60
Picric	lb.	.25	.25
Sulfanilic	lb.	.33	.33
Tobias'	lb.	2.25	2.25
Aminoazobenzene	lb.	1.15	1.15
Aniline Oil	lb.	.26	.26
For Red	lb.	.50	.50
Aniline Salt	lb.	.33	.33
Anthraquinone	lb.	3.00	2.50
Benzaldehyde, tech	lb.	.45	.45
U. S. P.	lb.	1.00	.80
Benzidine (Base)	lb.	1.00	1.00
Benzidine Sulfate	lb.	.80	.80
Diaminophenol	lb.	5.50	5.50
Dianisidine	lb.	8.00	8.00
p-Dichlorobenzene	lb.	.15	.15
Diethylaniline	lb.	1.50	1.50
Dimethylaniline	lb.	.90	.90
Dinitrobenzene	lb.	.29	.29
Dinitrotoluene	lb.	.43	.43
Diphenylamine	lb.	.80	.80
G Salt	lb.	.80	.80
Hydroquinone	lb.	2.00	1.90
Metol (Rhodol)	lb.	6.75	6.75
Monochlorobenzene	lb.	.14	.14
Monoethylaniline	lb.	2.15	2.15
α-Naphthylamine	lb.	.45	.45
β-Naphthylamine (Sublimed)	lb.	2.25	2.25
β-Naphthol, dist.	lb.	.45	.42
m-Nitroaniline	lb.	.90	.90
p-Nitroaniline	lb.	1.10	1.10
Nitrobenzene, crude	lb.	.14	.14
Rectified (Oil Mirbane)	lb.	.16	.16
p-Nitrophenol	lb.	.80	.80
p-Nitrosodimethylaniline	lb.	2.90	2.90
o-Nitrotoluene	lb.	.25	.25
p-Nitrotoluene	lb.	1.50	1.50
m-Phenylenediamine	lb.	1.30	1.30
p-Phenylenediamine	lb.	2.30	2.30
Phthalic Anhydride	lb.	.65	.65
Primuline (Base)	lb.	3.00	3.00
R Salt	lb.	.85	.85
Resorcinol, tech	lb.	2.25	2.00
U. S. P.	lb.	2.75	2.50
Schaeffer Salt	lb.	.75	.75
Sodium Naphthionate	lb.	1.10	1.10
Thiocarbanilide	lb.	.60	.60
Tolidine (Base)	lb.	1.75	1.75
Toluidine, mixed	lb.	.44	.44
o-Toluidine	lb.	.33	.33
m-Toluylenediamine	lb.	1.50	1.50
p-Toluidine	lb.	1.75	1.75
Xylidine, crude	lb.	.50	.45

COAL-TAR COLORS

Acid Colors

		Nov. 1	Nov. 15
Black	lb.	1.25	1.25
Blue	lb.	3.00	3.00

Acid Colors (*Concluded*)

		Nov. 1	Nov. 15
Fuchsin	lb.	2.50	2.50
Orange III	lb.	1.00	1.00
Red	lb.	1.30	1.30
Violet 10B	lb.	6.50	6.50
Alkali Blue, domestic	lb.	5.50	5.50
Imported	lb.	8.00	8.00
Azo Carmine	lb.	4.00	4.00
Azo Yellow	lb.	2.00	2.00
Erythrosin	lb.	12.00	12.00
Indigotin, conc	lb.	3.00	3.00
Paste	lb.	1.50	1.50
Naphthol Green	lb.	1.95	1.95
Ponceau	lb.	1.25	1.25
Scarlet 2R	lb.	1.00	1.00

Direct Colors

		Nov. 1	Nov. 15
Black	lb.	1.00	1.00
Blue 2B	lb.	.70	.70
Brown R	lb.	1.65	1.65
Fast Red	lb.	3.50	3.50
Yellow	lb.	2.00	2.00
Violet, conc	lb.	2.20	2.20
Chrysophenine, domestic	lb.	2.25	2.25
Imported	lb.	3.80	3.80
Congo Red, 4B Type	lb.	.90	.90
Primuline, domestic	lb.	3.00	3.00

Oil Colors

		Nov. 1	Nov. 15
Black	lb.	.70	.70
Blue	lb.	1.65	1.65
Orange	lb.	1.40	1.40
Red III	lb.	1.65	1.65
Scarlet	lb.	1.75	1.75
Yellow	lb.	1.70	1.70
Nigrosine Oil, soluble	lb.	.90	.90

Sulfur Colors

		Nov. 1	Nov. 15
Black	lb.	.20	.20
Blue, domestic	lb.	.70	.70
Brown	lb.	.35	.35
Green	lb.	1.00	1.00
Yellow	lb.	.90	.90

Chrome Colors

		Nov. 1	Nov. 15
Alizarin Blue, bright	lb.	7.75	7.75
Alizarin Red, 20% Paste	lb.	1.10	1.10
Alizarin Yellow G	lb.	1.00	1.00
Chrome Black, domestic	lb.	1.25	1.25
Imported	lb.	2.20	2.20
Chrome Blue	lb.	2.50	2.50
Chrome Green, domestic	lb.	2.00	2.00
Chrome Red	lb.	2.00	2.00
Gallocyanin	lb.	3.25	3.25

Basic Colors

		Nov. 1	Nov. 15
Auramine, O, domestic	lb.	2.50	2.50
Auramine, OO.	lb.	4.15	4.15
Bismarck Brown Y	lb.	.90	.90
Bismarck Brown R	lb.	1.20	1.20
Chrysoidine R	lb.	.75	.75
Chrysoidine Y	lb.	.75	.75
Green Crystals, Brilliant	lb.	6.00	6.00
Indigo, 20 p. c. paste	lb.	.85	.85
Fuchsin Crystals, domestic	lb.	6.50	6.50
Imported	lb.	12.00	12.00
Magenta Acid, domestic	lb.	4.25	4.25
Malachite Green, crystals	lb.	4.50	4.50
Methylene Blue, tech	lb	2.75	2.75
Methyl Violet 3 B	lb.	3.00	3.50
Nigrosine, spts. sol	lb.	.85	.85
Water sol., blue	lb.	.70	.70
Jet	lb.	.90	.90
Phosphine G., domestic	lb.	7.00	7.00
Rhodamine B, extra conc	lb.	40.00	40.00
Victoria Blue, base, domestic	lb.	6.00	6.00
Victoria Green	lb	6.00	6.00
Victoria Red	lb.	7.00	7.00
Victoria Yellow	lb.	7.00	7.00

AUTHOR INDEX

THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY
VOLUME XII—1920

AIKIN, V. L. Determination of Moisture in Beet-Sugar Factory Products.......... 979
Albrech, M. C. Determination of Crude Fiber in Prepared Mustard. 1175
Alexander, J. Colloidal Fuel. Note.......... 612
  Some Practical Applications of Colloidal Chemistry. Colloid Symposium, St. Louis Meeting, A. C. S.......... 434
Almy, L. H. and E. D. Clark. Chemical Study of Frozen Fish in Storage for Short and Long Periods.......... 656
Alsberg, C. L. Report, 36th Annual Convention, Association of Official Agricultural Chemists, Washington, D. C., November 17 to 19, 1919.......... 86
Alsberg, J. Heat Balance of a Distillation Plant for Recovery of Fatty Acids from Cottonseed Foots.......... 490
Ambler, J. A. Naphthalene Sulfonic Acids. I—Some Difficultly Soluble Salts of Certain Naphthalene Sulfonic Acids.......... 1081
  Naphthalene Sulfonic Acids. III—An Alternative Method for the Qualitative Detection of Naphthalene-2,7- and 1,6-Disulfonic Acids.......... 1194
  and W. J. Cotton. Use of Catalysts in the Sulfonation of Aromatic Compounds.......... 968
  and E. T. Wherry. Naphthalene Sulfonic Acids. II—A Method for the Qualitative Detection of Some of the Naphthalene Sulfonic Acids.......... 1085
Anderson, E. and R. J. Nestell. Formation of the Double Salts of Calcium and Potassium Sulfates at 100° C.......... 243
Anderson, M. S. and W. H. Fry. Solid Phases Obtained by the Evaporation of Certain Soil Extracts.......... 663
Anderson, R. P. Gasoline from Natural Gas. I—Method of Removal.......... 547
  Gasoline from Natural Gas. III—Heating Value, Specific Gravity, and Specific Heat, 852; Correction.......... 1028
  Gasoline from Natural Gas. IV—Temperature Correction and Blending Charts, 1011; Correction.......... 1214
  and C. E. Hinckley. Gasoline from Natural Gas. II—Use of Charcoal in Determining the Gasoline Content of Natural Gas.. 735
Arenson, S. B. and W. A. Felsing. Precipitation of Sulfur from Crude Mustard Gas by Means of Ammonia.......... 1065
  W. A. Felsing and F. J. Kopp. Method for Determining the Sulfur Monochloride Content of Mustard Gas-S_2Cl_2 Mixtures.......... 1054

BADGER, W. L. Determination of Oxygen by the Copper-Ammonia-Ammonium Chloride Reagent.......... 161
Bailey, C. H. Hygroscopic Moisture of Flour Exposed to Atmospheres of Different Relative Humidity.......... 1102
Bailey, H. S. and W. D. Baldsiefen. Detection of Oils other than Linseed in Paints, by Means of the Hexabromide Number of the Fatty Acids.......... 1189
  and C. B. Edwards. Determination of the Specific Heat of Heavy Mineral Oils.......... 891
Baker, F. P. and W. K. Lewis. Diffusing Power of Pigments.......... 890
Baker, G. C. Preparation of Ammonia-Free Water.......... 798
  and R. E. Greenfield. Relationship of Hydrogen-Ion Concentration of Natural Waters to Carbon Dioxide Content, 989; Correction.......... 1214
Baldsiefen, W. D. and H. S. Bailey. Detection of Oils other than Linseed in Paints, by Means of the Hexabromide Number of the Fatty Acids.......... 1189
Bancroft, W. D. Colloids in Biology and Medicine, by Bechhold. (Book Review).......... 412
  National Research Council. Report of the Chairman at the Annual Meeting of the Division of Chemistry and Chemical Technology. (*See* Editorial, 835).......... 911
Barsky, G. Fuel Value of Volatile Liquid Mixtures.......... 77
Bartow, E. Water Supply of the American Expeditionary Forces... 903
Baskerville, C. Chlorine and Influenza.......... 293
  Hygienic Control of the Aniline Dye Industry in Europe.......... 393
  Lead Coated Iron.......... 152
  Report of Committee on Occupational Diseases in the Chemical Trades. St. Louis Meeting, A. C. S.......... 439
  Utilization of Asphaltic Base Acid Sludge Obtained in Refining Petroleum and Shale Oils.......... 30
  Wood Alcohol—Coöperative Caution.......... 81
  Wood Alcohol No Longer: Hereafter Methanol.......... 910
Baude, W. A., L. H. Milligan and H. G. Boyd. Preparation of Arsenic Trichloride from White Arsenic and Phosgene.......... 221
Baughman, W. F. and W. W. Skinner. Determination of Iodide and Bromide in Mineral Waters and Brines.......... 358
Bayard, F. W., W. W. King and F. H. Rhodes. Use of Paracoumarone Resin in Varnishes.......... 549
Beal, G. D. and M. C. Perry. Quantities of Preservatives Necessary to Inhibit and Prevent Alcoholic Fermentation and Growth of Molds.......... 253
Bedford, C. W. and W. Scott. Reactions of Accelerators during Vulcanization.......... 31
Bennett, H. S. Chemical Market in India.......... 395
Benson, H. K. and R. E. Canfield. Low Temperature Distillation of Sub-bituminous Coal.......... 443
Berry, R. M. Rapid and Systematic Method for the Analysis of Light Aluminium Castiug Alloys.......... 998
Bertolet, E. C. Chemistry for Textile Students, by North and Blank. (Book Review).......... 1224
Bezzenberger, F. K. Evaluation of Aluminium Dross.......... 78
Bigelow, W. D. Report of Committee on Guaranteed Reagents and Standard Apparatus. St. Louis Meeting, A. C. S.......... 439
  Report of Committee to Formulate Specifications for the Construction of a Polariscope for Laboratory Use. St. Louis Meeting, A. C. S.......... 440
Bisson, C. S. and A. W. Christie. Note on the Solubility of Benzidine Sulfate in Water.......... 485
  Rapid Method for the Determination of Sulfur in Petroleum Oils.. 171
Black, J. H. and T. G. Thompson. Intersolubility of Chloropicrin and Water.......... 1066
Blair, A. W. Relative Availability of Nitrate Nitrogen and Commercial Organic Nitrogen. Field and Cylinder Experiments.... 262
Blake, A. F. Changes in the Polarizing Constants of Sugars during Refining.......... 1104
Blanco, G. W. and E. C. Sherrard. Acid Hydrolysis of Sugar-Cane Fiber and Cottonseed Hulls.......... 1160
Blasdale, W. C. Equilibria in Solutions Containing Mixtures of Salts. II—The System Water and the Chlorides and Sulfates of Sodium and Magnesium at 25°.......... 164
Bleininger, A. V. Ceramic Processes Associated with Colloid Phenomena. Colloid Symposium, St. Louis Meeting, A. C. S.... 436
Bogert, M T. Presentation Address. Perkin Medal Award...... 184
Boyd, H. G., W. A. Baude and L. H. Milligan. Preparation of Arsenic Trichloride from White Arsenic and Phosgene.......... 221
Boyle, C. L. Indicators Used for Determining Free Acid in Pickling Solutions.......... 571
Bradley, H. F. Rapid Determination of Small Amounts of C opper by the Iodide Method.......... 800
Bray, W. C., A. B. Lamb and J. C. W. Frazer. Removal of Carbon Monoxide from Air.......... 213
Brewer, R. E. and E. G. Mahin. Electrometric Method for Detecting Segregation of Dissolved Impurities in Steel.......... 1095
Brooks, B. T. Purchase of German Books and Periodicals.......... 394
Brown, K. Manufacture of Phenol in a Continuous High Pressure Autoclave.......... 279
Browne, C. A. Food Inspection and Analysis, by Leach and Winton. (Book Review).......... 828
  Testing of Saccharimeters by Means of the Telescopic Control Tube. 792
  The Bookplate of Dr. Joseph Priestley.......... 611
  The Question of the Identity of Balata and Gum Chicle.......... 199
Bryan, H. and R. O. E. Davis. Electrically Heated Bomb for Ammonia Synthesis.......... 287
Buchanan, G. H. and G. B. Winner. Solubility of Mono- and Diammonium Phosphate.......... 448
Burt, W. I., H. L. Trumbull, G. T. Sohl and S. G. Seaton. Control Experiments in Chloropicrin Manufacture. I—The Effect of Varying Quantities of Lime upon the Yield of Chloropicrin.. 1068
Bushnell, L. S. and H. S. Clark. Determination of Minute Quantities of Oil in Sulfur.......... 485
Bushong, F. W. and L. L. Knight. Specific Heat of Petroleum at Different Temperatures.......... 1197
Butt, C. A. Rapid and Accurate Method for Determining Nitrogen in Nitrate of Soda by the Modified Devarda Method and the Use of the Davisson Scrubber Bulb.......... 352
Butterman, S. Influence of the Method of Manufacture on the Use of Casein in Glue Making.......... 141
Byall, S., N. Kopeloff and L. Kopeloff. Effect of Concentration on the Deteriorative Activity of Mold Spores in Sugar.......... 256

CALDERWOOD, H. N., Jr. and L. F. Hawley. Tar-Still Operation in Hardwood Distillation Plants.......... 684
Caldwell, R. G. and H. C. Moore. Some Results of the Determination of Potash by the Lindo-Gladding Method.......... 1188
Camp, J. R. and J. W. Marden. Analysis of Molybdenum, Cobalt, and Chromium Alloys.......... 998
Campbell, A. Animal Fats and Oils, by Andés. (Book Review)... 1223
Campbell, C. H. Jelly.......... 558
Campbell, E. D. and G. F. Smith. Comparison of Accuracy in Analysis of Metallurgical Materials during the Past Twenty-Five Years.......... 1020
Canfield, R. E. and H. K. Benson. Low Temperature Distillation of Sub-bituminous Coal.......... 443
Caswell, W. W. Value of Cost Accounting in Commercial Laboratories.......... 79
Chandler, C. F. Address of Acceptance. Perkin Medal Award.... 189
  Presentation Address. Chandler Medal Award.......... 607
Chapin, E. S. Report to Dye Advisory Committee of the State Department, September 29, 1920. (*See* Editorial, 1042).......... 1130
Chapin, R. M. Diazometric Determination of Phenol, and of Certain of Its Homologs.......... 568
  New Method for the Determination of Phenol in the Presence of Certain Other Phenols.......... 771
Chase, W. S. Titration of Ammonium Acid Fluoride.......... 567
Chillas, R. B. and J. B. Hill. Electric Heater for the Coal-Tar Naphtha Distillation Test.......... 280
Christie, A. W. and C. S. Bisson. Rapid Method for the Determination of Sulfur in Petroleum Oils.......... 171
  Note on the Solubility of Benzidine Sulfate in Water.......... 485
Church, M. B. Laboratory Experiments on the Manufacture of Chinese Ang-Khak in the U. S.......... 45
Clark, C. M. Effective Connecting Bulb.......... 366
Clark, E. D. and L. H. Almy. Chemical Study of Frozen Fish in Storage for Short and Long Periods.......... 656
Clark, G. L. and R. B. Iseley. Studies on the Corrosive Action of Chlorine-Treated Water. I—The Effects of Steel on the Equilibrium: $Cl_2 + H_2O \rightleftharpoons HCl + HClO$, and of Products of the Equilibrium on Steel.......... 1116
Clark, H. S. and L. S. Bushnell. Determination of Minute Quantities of Oil in Sulfur.......... 485
Clark, W. M. Studies on Technical Casein. I—Introduction..... 1162
  H. F. Zoller, A. O. Dahlberg and A. C. Weimar. Studies on Technical Casein. II—Grain-Curd Casein.......... 1163
Clarke, W. F. and W. D. Collins. Use of Hydrogenated Oils in the Manufacture of Tin Plate.......... 149
Clemens, C. A. Insoluble Solids in Jams, Preserves, and Marmalades.......... 48
  New Type of Condenser for the Determination of Crude Fiber. (*See* Pickel, 611).......... 288

- Cochrane, D. C. Influence of Potassium Permanganate on Kjeldahl Nitrogen Determinations.... 1195
- Collins, W. D. Drawings of Standard Apparatus.... 817
  - Hardness of Surface Waters in the U. S.... 1181
  - Some American-Made Chemical Reagents.... 800
  - Standards and Tests for Reagent Chemicals, by Murray. (Book Review).... 1035
  - Unit Weights for Purchase of Reagents.... 1206
  - and W. F. Clarke. Use of Hydrogenated Oils in the Manufacture of Tin Plate.... 149
- Comey, A. M. Explosives, by Barnett. (Book Review).... 1035
- Cooledge, L. H. An Improved Comparator.... 499
- Coolidge, C., G. D. Kratz and A. H. Flower. Action of Certain Organic Accelerators in the Vulcanization of Rubber.... 317
- Cope, W. C. Strength and Velocity of Detonation of Various Military Explosives.... 870
- Cotton, W. J. and J. A. Ambler. Use of Catalysts in the Sulfonation of Aromatic Compounds.... 968
- Cottrell, F. G. Willard Gibbs Medal Address.... 697
- Cowan, W. A. Analysis of Babbitt, by Brakes. (Book Review).... 413
- Crane, E. J. An Opportunity to Obtain the London Chemical Society's Annual Reports on the Progress of Chemistry at a Reduced Rate.... 1213
  - Better Chemical Nomenclature in Trade Usage.... 1026
- Crossley, M. L. Qualifications of Organic Chemists. Address, Chicago Meeting, A. C. S.... 951
- Crosslev, T. L. Rapid Examination of Shellac, Shellac Varnish, and Lacquer.... 778

- DAHLBERG, A. O., W. M. Clark, H. F. Zoller and A. C. Weimar. Studies on Technical Casein. II—Grain-Curd Casein.... 1163
- Daniels, F., B. H. Kepner and P. P. Murdick. Heat of Hydration and Specific Heat of Wheat Flour.... 760
- Davis, H. S. and M. D. Davis. Detection of Arsenic in Sulfur.... 479
- Davis, R. O. E. Purification of Compressed Gases in Testing Catalysts for Ammonia Synthesis.... 289
  - and H. Bryan. Electrically Heated Bomb for Ammonia Synthesis. 287
  - and L. B. Olmstead. Preparation of Nitrogen and Hydrogen Mixture by Decomposition of Ammonia.... 316
- Davisson, B. S. On the Distillation of Ammonia.... 176
- Dean, E. W. and D. D. Stark. Convenient Method for the Determination of Water in Petroleum and Other Organic Emulsions. 486
- Dehn, W. M. and M. C. Tavlor. Chemical Method for the Detection in Fruit of a Prior Frozen Condition.... 977
- Demorest, D. J. The Making, Shaping, and Treating of Steel, by Camp and Francis. (Book Review).... 1226
- Dennis, L. M. Apparatus for the Determination of Melting Points.. 366
- Depew, H. A. and I. R. Ruby. Aging of Certain Rubber Compounds 1155
  - Some Microsections Cut from Vulcanized Rubber Articles.... 1156
- Deuel, H. J., Jr., and A. D. Holmes. Utilization of Kid, Rabbit, Horse, and Seal Meats as Food.... 975
- Dickerson, W. H. Millious from Waste, by Talbot. (Book Review).... 827
- Dixon, H. W. Method of Preparing Phloroglucinol Reagent for the Kreis Test.... 174
- Donleavy, J. J., T. B. Johnson and A. J. Hill. Some Catalysts Which Promote Reaction between Aniline and Ethyl Alcohol.... 636
- Dore, W. H. Determination of Cellulose in Woods, 264; Correction. 395
  - Distribution of Certain Chemical Constants of Wood over Its Proximate Constituents.... 472
  - Proximate Analysis of Coniferous Woods.... 476
  - Proximate Analysis of Hardwoods: Studies on *Quercus Agrifolia*.. 984
- Dorr, J. V. N. Manual of Cyanidation, by Hamilton. (Book Review).... 829
- Downs, C. R. and J. M. Weiss. Catalytic Oxidation. I—Benzene. 228
- DuBois, R. and H. I. Jones. Preservation of Eggs, Including a Bibliography of the Subject.... 751
- Durham, H., H. L. Trumbull and S. G. Seaton. Control Experiments in Chloropicrin Manufacture. II—Active Chlorine in the Sludge from the Manufacture of Chloropicrin.... 1068

- EDWARDS, C. B. and H. S. Bailey. Determination of the Specific Heat of Heavy Mineral Oils.... 891
- Eitel, E. H. American Progress in the Bacteriological Sugars.... 1202
- Englis, D. T. Note on the Use of Alundum Filtering Crucibles.... 799
- English, F. L. Analysis of Aromatic Nitro Compounds by Means of Titanous Chloride.... 994
- Esselen, G. J., Jr. Certain Aspects of the Chemistry of Cellulose Acetate from the Colloidal Viewpoint.... 801
  - Cellulose Symposium for the Chicago Meeting, A. C. S.... 814
- Euston, E. "Porcelain" White Lead.... 974

- FABER, H. B. and W. B. Stoddard. Short Commercial Analytical Methods for the Determination of Purity of Important Chemicals Used in Pyrotechnics.... 576
- Fay, H. Commercial Laboratory Notes, by Petty. (Book Review).. 309
  - Metallography. Part I, Principles of Metallography, by Hoyt. (Book Review).... 828
- Felsing, W. A. and S. B. Arenson. Precipitation of Sulfur from Crude Mustard Gas by Means of Ammonia.... 1065
  - S. B. Arenson and F. J. Kopp. Method for Determining the Sulfur Monochloride Content of Mustard Gas-S_2Cl_2 Mixtures... 1054
  - H. Odeen and C. B. Peterson. Decomposition of and Pressure Developed by Mustard Gas in Steel Shell at 60° C.... 1063
- Ferris, L. W. Volumetric Method for the Detection and Estimation of Neutralizers in Butter and in Certain Allied Products.... 757
- Feuer, B. and J. H. Reedv. Corrosion of Brass in Dilute Electrolytes 541
  - and F. W. Tanner. Action of Ultraviolet Light on the Yeast-Like Fungi—I.... 740
- Flohil, J. T. Volumetric Method for the Determination of Diastatic Capacity.... 677
- Flower, A. H. and G. D. Kratz. Effect of Certain Accelerators upon the Properties of Vulcanized Rubber—II.... 971
  - G. D. Kratz and C. Coolidge. Action of Certain Organic Accelerators in the Vulcanization of Rubber.... 317
- Foote, H. E. and G. W. Heise. Production of Ammonia and Formates from Cyanides, Ferrocyanides, and Cyanized Briquets.... 331
- Franklin, N. E. "Crippling a Great Work." (*See* Editorials, 835, 1042).... 1132
- Frantz, H. W., E. R. Weaver, P. E. Palmer, P. G. Ledig and S. F. Pickering. Automatic Methods of Gas Analysis Depending upon Thermal Conductivity. (*See* Shakespear, 1027).... 359
- Frazer, J. C. W., A. B. Lamb and W. C. Bray. Removal of Carbon Monoxide from Air.... 213
- Frieden, A. and A. W. Thomas. Determination of Hydrochloric Acid and Neutral Chlorides in Leather.... 1186
- Fries, A. A. Chemical Warfare. Address, St. Louis Meeting, A. C. S.... 423
- Fry, W. H. and M. S. Anderson. Solid Phases Obtained by the Evaporation of Certain Soil Extracts.... 663
- Fuller, A. V. Modified Form of the Smith Fermentation Tube.... 595

- GANGLOFF, W. C. Melting Point of Sodium Nitrite. Note.... 613
- Garby, C. D. and J. A. LeClerc. Pearl Barley: Its Manufacture and Composition.... 451
- Gardner, H. A. White Lead—Its Use in Paint, by Sabin. (Book Review).... 517
- Gibbs, H. D. History of the Preparation and Properties of Pure Phthalic Anhydride.... 1017
  - Production of Hydrochloric Acid from Chlorine and Water.... 538
  - and M. Phillips. Alkali Fusions. I—The Fusion of Sodium *p*-Cymene Sulfonate with Sodium Hydroxide for the Production of Carvacrol. (*See* Hixson and McKee, 296).... 145
    - Alkali Fusions. II—The Fusion of Sodium Benzene *m*-Disulfonate with Sodium Hydroxide for the Production of Resorcinol 857; Correction.... 1028
    - Purification of Benzoic Acid by Fractional Condensation.... 277
    - Synthesis of Thymol from *p*-Cymene.... 733
- Goldstein, A. E. and L. McMaster. Modification of the Thompson Method for the Determination of Acetic Acid in White Lead. 170
- Goodwin, L. F. and E. T. Sterne. Losses Incurred in the Preparation of Acetone by the Distillation of Acetate of Lime.... 240
- Graber, H. T. The Yeasts, by Guilliermond. (Book Review).... 1225
- Gray, G. W. The Petroleum Handbook, by Andros. (Book Review).... 516
- Gray, H. LeB. Fire Caused by Yellow Phosphorus. Note.... 199
- Greenfield, R. E. and G. C. Baker. Relationship of Hydrogen-Ion Concentration of Natural Waters to Carbon Dioxide Content, 989; Correction.... 1214
- Griffin, R. C. Solubility of Metals in Acids Containing Formaldehyde.... 1159
- Grissom, J. T. Formaldehyde Method for Determining Ammonium Nitrate.... 172
- Grotlisch, V. E. Determination of Acetic Acid in Pyroligneous Acid.... 1183
- Gudeman, E. Reconstruction Aspects of Some Chemical Industries in the U. S.... 376
- Guppy, C. M. New Publications.....103, 206, 310, 414, 518, 622, 726

- HALE, H. Chlorine as a Preventive of Influenza.... 80
- Hale, W. J. Plan for Incentive to Research in Pure and Applied Chemistry.... 690
- Halverson, J. O. and J. A. Schulz. McCrudden Gravimetric Calcium Method Modified.... 77
- Hamilton, H. C. Chemistry of Digitalis.... 1180
  - Purified Cresol (Cresylic Acid). (*See* York, 296).... 50
- Hamlin, M. L. Examination of the College Trained Chemist for Government Service. (*See* This Journal, **11** (1919), 1142).... 89
- Hamor, W. A. Annual Reports of the Society of Chemical Industry on the Progress of Applied Chemistry. (Book Review).... 1036
  - David Shepard Pratt. Obituary.... 400
  - Leonard Merritt Liddle. Obituary.... 400
  - L. C. Newell, A. M. Patterson and W. Segerblom. Chemical Reading Courses. (*See* McClelland, 1026)....701, 806
- Harger, R. N. Changes Taking Place in Cyanamid when Mixed with Fertilizer Materials.... 1111
  - Dicyanodiamide: A Rapid, Direct Method for Its Determination in Cyanamid and Mixed Fertilizers.... 1107
- Harrington, J. W. All Ready for the St. Louis Meeting, A. C. S... 395
  - In the Alembic of Publicity.... 705
  - Setting the Scenes for the Chicago Meeting, A. C. S.... 918
  - The A. C. S. News Service Report.... 196
- Harris, J. B. and G. P. Meade. Hess-Ives Tint-Photometer and Its Use with Raw Sugars.... 686
- Harrison, A. P. and F. M. Scales. Boric Acid Modification of the Kjeldahl Method for Crop and Soil Analysis.... 350
- Hart, M. C. and A. D. Hirschfelder. Simple Method for the Preparation of Sodium Amalgam in Flakes.... 499
- Hartwig, E. H. and E. G. Mahin. Inclusions and Ferrite Crystallization in Steel. II—Solubility of Inclusions.... 1090
- Hasche, R. L., A. M. Pardee and E. E. Reid. Butyl Alcohol as a Medium for the Determination of Saponification Numbers.... 481
- Hawley, L. F. Numerical Relation between Cells and Treatments in Extraction Processes, 493; Correction.... 613
  - and H. N. Calderwood, Jr. Tar-Still Operation in Hardwood Distillation Plants.... 684
- Havnes, W. Annuario per le Industrie Chimiche e Farmaceutiche—Anno I, 1918, by Nasini, *et al.* (Book Review).... 413
- Heath, F. H. and W. L. Semon. Reaction between Selenium Monochloride and Ethylene..... 1100
- Heise, G. W. and H. E. Foote. Production of Ammonia and Formates from Cyanides, Ferrocyanides, and Cyanized Briquets.... 331
- Herschel, W. H. MacMichael Torsional Viscosimeter. (*See* MacMichael, 817).... 282
- Herty, C. H. Opening Address, Sixth National Exposition of Chemical Industries.... 956
  - Victory and Its Responsibilities. Address, St. Louis Meeting, A. C. S.... 429

Editorials:
  - A House Built upon a Rock.... 4
  - Air-Castles.... 315
  - A Life of Service.... 211
  - An Unfinished Story.... 627
  - A Significant Combination.... 107
  - Canadian Hospitality.... 626
  - Caught Up.... 1147
  - Chairman Bancroft's Report.... 835
  - Chapin Report.... 1042
  - Chemical Warfare Service.... 314
  - Chemical Warfare Service Endangered.... 2
  - Chicago Meeting.... 730
  - Crippling a Great Work.... 835
  - Critical Days.... 107
  - Dr Manning Retires.... 524

  Dyes in the Senate.... 210
  Evolution in Alcohol Administration.... 1044
  From the Senate Gallery.... 522
  Help Wanted.... 522
  How Best to Serve.... 731
  Hurry Call.... 1146
  Inadequate Patent Service.... 212
  Increase in Dues.... 834
  In the Game.... 1147
  Kicking Up Dust.... 3
  Lost Ground to Be Recovered.... 210
  Lying Down on the Job.... 1042
  Machinery Installed—Lubrication Next.... 1147
  Mutual Obligations.... 836
  Notes.... 109, 212, 315, 524, 628, 732, 1044, 1148
  "Nothing to Eat but Food".... 314
  Officers for 1920.... 2
  One-Sided Greasing.... 626
  Playing Their Game.... 1146
  Potash from a New Angle.... 834
  President-Elect Harding's Views.... 1146
  Professor Bogert Declines.... 731
  Prophetic.... 731
  Relief for the Patent Office.... 314
  Rope Making.... 626
  Safety in Speech.... 109
  St. Louis Next.... 210
  Student Opinion.... 108
  Substance Rather than Shadow.... 1043
  The Joy and the Sorrow of M. I. T.... 108
  The Masquerading Filter Paper.... 1043
  To Your Post.... 730
Higgins, E. F. and E. C. Pitman. Measurement of Viscosity of Pyroxylin Solutions.... 587
Hill, A. J., T. B. Johnson and J. J. Donleavy. Some Catalysts Which Promote Reaction between Aniline and Ethyl Alcohol.... 636
Hill, J. B. and R. B. Chillas. Electric Heater for the Coal-Tar Naphtha Distillation Test.... 280
Hinckley, C. E. and R. P. Anderson. Gasoline from Natural Gas. II—Use of Charcoal in Determining the Gasoline Content of Natural Gas.... 735
Hirschfelder, A. D. and M. C. Hart. Simple Method for the Preparation of Sodium Amalgam in Flakes.... 499
Hixson, A. W. and R. H. McKee. Alkali Fusions. I—The Fusion of Sodium *p*-Cymene Sulfonate with Sodium Hydroxide for the Production of Carvacrol. (*See* Gibbs and Phillips, 145).... 296
Hoguet, R. The Chemical Foundation, Inc., Patents.... 297
Holmes, A. D. and H. J. Deuel, Jr. Utilization of Kid, Rabbit, Horse, and Seal Meats as Food.... 975
Holmes, H. N. The Second Report on Colloidal Chemistry and Its General and Industrial Applications, 1918. (Book Review).... 101
Holmes, W. C. Freezing Points of Mixtures of Sulfuric and Nitric Acids.... 781
Holstein, P. F. Potassium Nitrate from the Chilean Nitrate Industry.... 290
Holz, H. A. Franklin Filter Paper. (*See* Editorials, 955, 1042).... 1132
Hopkins, O. P.:
  Chemical Industry and Trade of Italy.... 525
  Chemical Industry and Trade of Japan.... 110
  Chemical Industry and Trade of Norway.... 632
  Chemical Industry and Trade of Spain.... 223, 298
  Chemical Industry and Trade of Sweden.... 1045
  Our Foreign Trade in Chemicals.... 840
Hopp, G. Determination of the Tensile Strength of Glue.... 356
Horne, W. D. Bone-Black and Decolorizing Carbons.... 1015
  Recent Advances in Defecation.... 1179
Houseman, P. A. and C. K. Swift. Preparation of Hematoxylin.... 173
Howe, H. E. Creative Chemistry, by Slosson. (Book Review).... 516
  Report of Committee Appointed to Define the Field Covered by Respective Divisions and Sections of the A. C. S. St. Louis Meeting, A. C. S.... 438
Hoyt, L. F. and G. W. Rolfe. Notes on Double Polarization Methods for the Determination of Sucrose and a Suggested New Method.... 250
Huff, W. J. Cause and Prevention of After-Corrosion on the Bores of Firearms.... 862
Hulett, G. A. and O. A. Nelson. Moisture Content of Cereals.... 40
Hults, W. L. and E. Little. Rapid Accurate Method for the Analysis of an Iron Ore.... 269

Iseley, R. B. and G. L. Clark. Studies on the Corrosive Action of Chlorine-Treated Water. I—The Effects of Steel on the Equilibrium: $Cl_2 + H_2O \rightleftharpoons HCl + HClO$, and of Products of the Equilibrium on Steel.... 1116

Jacobs, B. R. and O. S. Rask. Laboratory Control of Wheat Flour Milling.... 899
Jarrell, T. D. and F. P. Veitch. Determination of the Water Resistance of Fabrics.... 26
Johnson, T. B., A. J. Hill and J. J. Donleavy. Some Catalysts Which Promote Reaction between Aniline and Ethyl Alcohol.... 636
Johnston, J. Catalysis in Industrial Chemistry, by Henderson. (Book Review).... 101
Jones, G. Progress of the American Coal-Tar Chemical Industry during 1919. Address, Chemical Exposition.... 959
Jones, H. I. and R. DuBois. Preservation of Eggs, Including a Bibliography of the Subject.... 751
Jordan, H. W. Responsibilities of the Chemist as a Citizen.... 629

Kaplan, B. B. and W. A. Selvig. Hygroscopicity of By-Product Coke.... 783
Kasanof, D. R. Notes on the Preparation of Cupferron.... 799
Kebler, L. F. A Study of the Economic Status of Chemists in the Government Service, Ten Educational Institutions and Thirty-seven Firms.... 1206
Keenan, T. J. Modern Pulp and Paper Making, by Witham. (Book Review).... 1225
  Technical Association of the Pulp and Paper Industry. Announcement.... 815
Keitt, T. E. DeRoode-Perchloric Acid Method for Determining Potash.... 276
Kelly, W. J. Determination of True Free Sulfur and the True Coefficient of Vulcanization in Vulcanized Rubber.... 875
Kepner, B. H., F. Daniels and P. P. Murdick. Heat of Hydration and Specific Heat of Wheat Flour.... 760
Kerbs, R. H. Explosion of Flashlight Powders.... 1026
Kern, E. J. Determination of Sulfate in Sulfonated Oils.... 785
  and J. A. Wilson. Nature of the Hide-Tannin Compound and Its Bearing upon Tannin Analysis.... 1149
  True Tanning Value of Vegetable Tanning Materials.... 465
King, W. W., F. W. Bayard and F. H. Rhodes. Use of Paracoumarone Resin in Varnishes.... 549
Kiplinger, C. C. Substitutes for Platinum Wire in Bead and Flame Tests.... 500
Knight, H. G. Acidity and Acidimetry of Soils. I—Studies of the Hopkins and Pettit Method for Determining Soil Acidity.... 340
  Acidity and Acidimetry of Soils. II—Investigation of Acid Soils by Means of the Hydrogen Electrode.... 457
  Acidity and Acidimetry of Soils. III—Comparison of Methods for Determining Lime Requirements of Soils with Hydrogen Electrode. IV—Proposed Method for Determination of Lime Requirements of Soils.... 559
Knight, L. L. and F. W. Bushong. Specific Heat of Petroleum at Different Temperatures.... 1197
Knowles, C. L. Some Physical Constants of Pure Aniline.... 881
  Stability of Tetryl.... 246
Knowles, H. B. and G. E. F. Lundell. Determination of Zirconium in Steel.... 562
  Use of Cupferron in Quantitative Analysis.... 344
Kohr, A. A. Rapid Method for Quantitative Determination of Arsenic in Commercial Sulfuric Acid.... 580
Kopeloff, L., N. Kopeloff and S. Byall. Effect of Concentration on the Deteriorative Activity of Mold Spores in Sugar.... 256
Kopeloff, N. Effect of Varying the Amount of Inoculum and Concentration on the Deterioration of Sugar by Molds.... 455
  Prevention of Sugar Deterioration by the Use of Superheated Steam in Centrifugals, 860; Correction.... 1028
  S. Byall and L. Kopeloff. Effect of Concentration on the Deteriorative Activity of Mold Spores in Sugar.... 256
  and H. Z. E. Perkins. Deterioration of Cuban Raw Sugars in Storage.... 555
Kopp, F. J. and T. G. Thompson. Pressures Produced by the Action of Sulfur Monochloride upon β,β'-Dichloroethyl Sulfide.... 1056
  W. A. Felsing and S. B. Arenson. Method for Determining the Sulfur Monochloride Content of Mustard Gas-S_2Cl_2 Mixtures.... 1054
Kratz, G. D. and A. H. Flower. Effect of Certain Accelerators upon the Properties of Vulcanized Rubber—II.... 971
  A. H. Flower and C. Coolidge. Action of Certain Organic Accelerators in the Vulcanization of Rubber.... 317
Krauskopf, F. C. and L. H. Purdy. Convenient Method for the Preparation of a Hydrochloric Acid Solution of Cuprous Chloride for Use in Gas Analysis.... 158
Kremers, E. New Fields of Phytochemical Research Opened up by the Cultivation of Medicinal Plants on an Economic Scale.... 1018

Lamb, A. B., W. C. Bray and J. C. W. Frazer. Removal of Carbon Monoxide from Air.... 213
Langmuir, I. Address of Acceptance. Structure of Atoms and Its Bearing on Chemical Valence. Nichols Medal Award.... 386
Law, T. C. Report of the Committee on Cottonseed Products, Division of Industrial and Engineering Chemistry, A. C. S.... 707
LaWall, C. H. Relation of the Chemist to the United States Pharmacopoeia.... 696
LeClerc, J. A. and C. D. Garby. Pearl Barley: Its Manufacture and Composition.... 451
Ledig, P. G. Inflammability of Jets of Hydrogen and Inert Gas.... 1098
  and E. R. Weaver. New Forms of Combustion Apparatus for Use in Gas Analysis.... 368
  E. R. Weaver, P. E. Palmer, H. W. Frantz and S. F. Pickering. Automatic Methods of Gas Analysis Depending upon Thermal Conductivity. (*See* Shakespear, 1027).... 359
Lenher, V. Selenium and Tellurium.... 597
Leo, S. T. and R. H. McKee. Continuous Process for Electrolytic Regeneration of Chromic Acid.... 16
Levey, H. A. Cellulose Phthalate: Its Preparation and Properties. 743
Levine, B. S. and F. P. Veitch. Testing the Mildew Resistance of Textiles.... 139
Lewis, W. K. Vapor Composition of Alcohol-Water Mixtures.... 496
  and F. P. Baker. Diffusing Power of Pigments.... 890
  and W. H. McAdams. Direct Method for the Determination of Rubber Hydrocarbon in Raw and Vulcanized Rubber.... 673
Lind, S. C. Practical Methods for the Determination of Radium. III—Alpha-Ray Method, Gamma-Ray Method, Miscellaneous.... 469
Little, E. and W. L. Hults. Rapid Accurate Method for the Analysis of an Iron Ore.... 269
Loevenhart, A. S. Chemistry's Contribution to the Life Sciences. Address, Chicago Meeting, A. C. S.... 1122
Lomanitz, S. Oil of the Prickly Pear Seed.... 1175
Lormand, C. International Chemical Conference.... 925
  Paris Letter.... 820, 1029, 1134, 1217
Low, W. H. Soy-Bean Oil.... 572
  Testing the Strength of Glue Jellies.... 355
  Unsaponifiable Matters. (*See* This Journal, **11** (1919), 1161).... 713
Lowy, A. Fire Caused by Yellow Phosphorus.... 507
Lubs, H. A. Indicators and Their Industrial Application.... 273
Lundell, G. E. F. and H. B. Knowles. Determination of Zirconium in Steel.... 562
  Use of Cupferron in Quantitative Analysis.... 344
Lyford, C. A. Chemical Preparedness.... 506

MacMichael, R. F. MacMichael Torsional Viscosimeter. (*See* Herschel, 282).... 817
MacMillan, A. M. and A. Tingle. Acidimetry of Red Wines and Fruit Juices.... 274
Mahin, E. G. and E. H. Hartwig. Inclusions and Ferrite Crystallization in Steel. II—Solubility of Inclusions.... 1090
  and R. E. Brewer. Electrometric Method for Detecting Segregation of Dissolved Impurities in Steel.... 1095
Mahood, S. A. Some Observations on the Determination of Cellulose in Woods.... 873
  Thermal Decomposition of Turpentine with Particular Reference to the Production of Toluene and Isoprene.... 1152
Malcolmson, J. D. Colloidal Method for Increasing the Volume of Adhesive Water-Glass.... 174

Marden, J. W. and J. R. Camp. Analysis of Molybdenum, Cobalt, and Chromium Alloys.......... 998
and M. N. Rich. Investigations on Zirconium.......... 651
Marshall, J. Manufacture of Trinitroxylene for Use as a Substitute for TNT in Bursting Charges for High Explosive Shell.......... 248
Preparation of Hexanitrodiphenylamine and Its Use as a Booster for Shell Charges.......... 336
Mathewson, W. E. Detection and Estimation of Yellow AB and Yellow OB in Mixtures.......... 883
Matthews, J. M. From Newton to Einstein, by Harrow. (Book Review).......... 725
McAdams, W. H. and W. K. Lewis. Direct Method for the Determination of Rubber Hydrocarbon in Raw and Vulcanized Rubber.......... 673
McBride, R. S. Government Publications..........96, 204, 303
McClelland, E. H. Chemical Reading Courses. (*See* Hamor, *et al.*, 701, 806).......... 1026
McCullough, J. C. Welding Thermocouples in the Electric Arc... 903
McCune, J. S. and A. N. Thurston. Preservatives for Fermentable Beverage Samples.......... 689
McDonnell, J. B. Washington Letter..........90, 200, 299, 398, 507, 613, 718, 818, 926, 1028, 1133, 1215
McHargue, J. S. Cause of Deterioration and Spoiling of Corn and Corn Meal.......... 257
McIlhiney, P. C. Hydrogenation of Oils, by Ellis. (Book Review).......... 309
McKee, R. H. Introductory Remarks. Chandler Medal Award... 599
and A. W. Hixson. Alkali Fusions. I—The Fusion of Sodium *p*-Cymene Sulfonate with Sodium Hydroxide for the Production of Carvacrol. (*See* Gibbs and Phillips, 145).......... 296
and S. T. Leo. Continuous Process for Electrolytic Regeneration of Chromic Acid.......... 16
McMaster, L. and A. E. Goldstein. Modification of the Thompson Method for the Determination of Acetic Acid in White Lead.... 170
McMillan, A. Foreign Industrial News..........82, 181, 389
McPherson, W. Improvement of Conditions for College Instructing Staffs.......... 813
Treatise on General and Industrial Inorganic Chemistry, by Molinari. (Book Review).......... 1036
Meade, G. P. and J. B. Harris. Hess-Ives Tint-Photometer and Its Use with Raw Sugars.......... 686
Miall, S. London Letter..........819, 928, 1216
Miller, H. M. Modification of the Howard Method for Counting Yeasts, Spores, and Bacteria in Tomato Products.......... 766
Milligan, L. H., W. A. Baude and H. G. Boyd. Preparation of Arsenic Trichloride from White Arsenic and Phosgene.......... 221
Monroe, K. P. Phthalic Anhydride. IV—The Vapor Pressure of Phthalic Anhydride.......... 969
Moody, H. R. Military Pyrotechnics, by Faber. (Book Review).. 828
Moore, H. C. Determination of Nitrate Nitrogen in Nitrates and Fertilizers.......... 669
and R. G. Caldwell. Some Results of the Determination of Potash by the Lindo-Gladding Method.......... 1188
Murdick, P. P., F. Daniels and B. H. Kepner. Heat of Hydration and Specific Heat of Wheat Flour.......... 760
Murphy, T. H. Sugar Industry of France since the War.......... 1124

NELSON, E. M. Chemical Study of the Ether Extracts of Soy-Bean Leaves.......... 49
Nelson, O. A. and G. A. Hulett. Moisture Content of Cereals.... 40
Nestell, R. J. and E. Anderson. Formation of the Double Salts of Calcium and Potassium Sulfates at 100° C.......... 243
Newell, L. C., W. A. Hamor, A. M. Patterson and W. Segerblom. Chemical Reading Courses. (*See* McClelland, 1026)......701, 806
Newhall, C. A. Direct Identification of Soy-Bean Oil.......... 1174
Nichols, M. S. Nitrate Content of Certain Waters Considered Bacteriologically Safe.......... 987
Nichols, W. H. Presentation Address. Nichols Medal Award.... 385
Nicolet, B. H. Some Anomalies in the Solidification Point of Tristearin.......... 741
The Uniform Composition of Commercial "Stearic" Acids, and Its Explanation.......... 677
Noyes, W. A. Introductory Address, St. Louis Meeting, A. C. S.... 423
Report of Committee on Coöperation between Universities and Industries. St. Louis Meeting, A. C. S.......... 439
Nutting, P. G. The Organization of Industrial Scientific Research, by Mees. (Book Review).......... 1037

ODEEN, H., W. A. Felsing and C. B. Peterson. Decomposition of and Pressure Developed by Mustard Gas in Steel Shell at 60° C. 1063
and T. G. Thompson. Solubility of β,β′-Dichloroethyl Sulfide in Petroleum Hydrocarbons and Its Purification by Extraction with These Solvents.......... 1057
Olmstead, L. B. and R. O. E. Davis. Preparation of Nitrogen and Hydrogen Mixture by Decomposition of Ammonia.......... 316
Olney, L. A. Dyeing with Coal-Tar Dyestuffs, by Whittaker. (Book Review).......... 309
Olsen, J. C. Chemical Calculation Tables, by Wells. (Book Review).......... 516
Reports of American Institute of Chemical Engineers:
12th Annual Meeting, Savannah, Ga., December 2 to 6, 1919.... 85
12th Semi-Annual Meeting, Canada, June 28 to July 3, 1920.... 812
O'Neill, E. The Profession of Chemistry, by Pilcher. (Book Review).......... 1035
Ort, J. M. and J. R. Withrow. Sugar Sirup from Home-Grown Sugar Beets.......... 154
Osborn, S. J. Chemical Control of the Beet Sugar Industry.......... 803
Oshima, K. New Technical Method for the Estimation of the Saccharogenic Power of Diastatic Preparations.......... 991

PALKIN, S. Behavior of Phenolphthalein with Iodine and a Method for the Determination of Phenolphthalein.......... 766
Palmer, P. E. and E. R. Weaver. Application of the Thermal Conductivity Method to the Automatic Analysis of Complex Mixtures of Gases.......... 894
E. R. Weaver, H. W. Frantz, P. G. Ledig and S. F. Pickering. Automatic Methods of Gas Analysis Depending upon Thermal Conductivity. (*See* Shakespear, 1027).......... 359
Pardee, A. M., R. L. Hasche and E. E. Reid. Butyl Alcohol as a Medium for the Determination of Saponification Numbers...... 481
and E. E. Reid. Influence of Ester Transposition in the Determination of Saponification Numbers.......... 129
Parkinson, N. A. Government Publications..........406, 511, 617, 722, 823, 930, 1032, 1138, 1220
Parr, S. W. Liquid Fuel for Internal Combustion Engines, by Moore. (Book Review).......... 309
Parsons, C. L.
Advisory Committee Minutes, A. C. S.......... 84
Impressions of the Italian Chemical Industry.......... 907
Patterson, A. M. Condensed Chemical Dictionary. *Edited* by Turner, *et al.* (Book Review)..........102, 725
W. A. Hamor, L. C. Newell and W. Segerblom. Chemical Reading Courses. (*See* McClelland, 1026)..........701, 806
Pearce, W. T. Wearing Quality of Exterior Varnishes Compared with Their Physical and Chemical Analyses.......... 552
Perrins, H. Z. E. and N. Kopeloff. Deterioration of Cuban Raw Sugars in Storage.......... 555
Perley, G. A. Commercial Oxidation of Ammonia..........5, 119
Perrott, G. St. J. and R. Thiessen. Carbon Black—Its Properties and Uses.......... 324
Perry, M. C. and G. D. Beal. Quantities of Preservatives Necessary to Inhibit and Prevent Alcoholic Fermentation and the Growth of Molds.......... 253
Peterson, C. B., W. A. Felsing and H. Odeen. Decomposition of and Pressure Developed by Mustard Gas in Steel Shell at 60° C.......... 1063
Phelps, I. K. Report of the Committee on Endowment of the A. C. S. St. Louis Meeting, A. C. S.......... 442
Phillips, M. and H. D. Gibbs. Alkali Fusions. I—The Fusion of Sodium *p*-Cymene Sulfonate with Sodium Hydroxide for the Production of Carvacrol. (*See* Hixon and McKee, 296).......... 145
Alkali Fusions. II—The Fusion of Sodium Benzene *m*-Disulfonate with Sodium Hydroxide for the Production of Resorcinol, 857; Correction.......... 1028
Purification of Benzoic Acid by Fractional Condensation.......... 277
Synthesis of Thymol from *p*-Cymene.......... 733
Pickel, J. M. New Type of Condenser for the Determination of Crude Fiber. (*See* Clemens, 288).......... 611
Pickering, S. F., E. R. Weaver, P. E. Palmer, H. W. Frantz and P. G Ledig. Automatic Methods of Gas Analysis Depending upon Thermal Conductivity. (*See* Shakespear, 1027).......... 359
Pickett, O. A. New Method for the Determination of Acetic Acid in Acetates.......... 570
Pierlé, C. A. Analytical Chemistry of Uranium and Its Separation from Other Rare Elements.......... 60
Pitman, E. C. and E. F. Higgins. Measurement of Viscosity of Pyroxylin Solutions.......... 587
Pond, F. J. Boiler Feed Water, by Jackson. (Book Review)...... 829
Poore, H. D. Orange Vinegar: Its Manufacture and Composition.......... 1176
Powell, A. R. Study of the Reactions of Coal Sulfur in the Coking Process.......... 1069
Determination of Sulfur Forms in Coal.......... 887
Desulfurizing Action of Hydrogen on Coke.......... 1077
Purdy, L. H. and F. C. Krauskopf. Convenient Method for the Preparation of a Hydrochloric Acid Solution of Cuprous Chloride for Use in Gas Analysis.......... 158

RABAK, F. Effect of Mold upon the Oil in Corn.......... 46
Rask, O. S. and B. R. Jacobs. Laboratory Control of Wheat Flour Milling.......... 899
Rector, T. M. Lipolytic Enzymes in Olive Oil.......... 156
Reedy, J. H. and B. Feuer. Corrosion of Brass in Dilute Electrolytes 541
Reid, E. E. and A. M. Pardee. Influence of Ester Transposition in the Determination of Saponification Numbers.......... 129
A. M. Pardee and R. L. Hasche. Butyl Alcohol as a Medium for the Determination of Saponification Numbers.......... 481
Rhodes, F. H., W. W. King and F. W. Bayard. Use of Paracoumarone Resin in Varnishes.......... 549
Rice, F. E. New Conductivity Cell.......... 1202
Rice, H. I. and M. R. Walczak. Extraction of Bitumens from Mineral Aggregate.......... 738
Rich, M. N. and J. W. Marden. Investigations on Zirconium...... 651
Richards, J. W. Report, 37th Meeting, American Electrochemical Society.......... 503
Report, 38th Meeting, American Electrochemical Society.......... 1128
Richardson, W. D. Technical Handbook of Oils, Fats and Waxes. Vol. II—Practical and Analytical, by Fryer. (Book Review)... 516
Unsaponifiable Matters. (*See* This Journal, **11** (1919), 1161).... 715
Richmond, T. E., A. L. Whiting and W. R. Schoonover. Determination of Nitrates in Soil.......... 982
Rideal, E. K. On the Absorption of Oxides of Nitrogen by Nitric Acid.......... 531
Robinson, Charles S. and O. B. Winter. Electrometric Analysis of Arsenicals.......... 775
Robinson, Clark S. Effect of Air in Steam on the Coefficient of Heat Transmission, 644; Correction.......... 818
Rogers, A. Abstract, Address of Acceptance. Grasselli Medal Award 1128
Utilization of the Shark for Food and Leather.......... 293
Rolfe, G. W. and L. F. Hoyt. Notes on Double Polarization Methods for the Determination of Sucrose and a Suggested New Method.......... 250
Rose, R. E. Dye Research.......... 805
Education of the Research Chemist.......... 947
Ruby, I. R. and H. A. Depew. Aging of Certain Rubber Compounds.......... 1155
Some Microsections Cut from Vulcanized Rubber Articles.......... 1156
Ruhm, H. D. The United States' Search for Natural Deposits of Soluble Potash. (*See* Editorial, 834).......... 837

SANDERS, M. T. Effect of Chlorides on the Nitrometer Determination of Nitrates.......... 169
Sanderson, C. W. Expansion of Rubber Compounds during Vulcanization.......... 37
Scales, F. M. and A. P. Harrison. Boric Acid Modification of the Kjeldahl Method for Crop and Soil Analysis.......... 350
Schippel, H. F. Volume Increase of Compounded Rubber under Strain.......... 33
Schlatter, H. Note on Catalysis in the Manufacture of Ether..... 1101
Schoonover, W. R., A. L. Whiting and T. E. Richmond. Determination of Nitrates in Soil.......... 982
Schulz, J. A. and J. O. Halverson. McCrudden Gravimetric Calcium Method Modified.......... 77
Scott, J. W., Jr., S. E. Sheppard and S. S. Sweet. Jelly Strength of Gelatins and Glues, 1007; Correction.......... 1214

Scott, W. Application of the Rotating Zinc Reductor in the Determination of Molybdenum.... 578
  and C. W. Bedford. Reactions of Accelerators during Vulcanization.... 31
Scoville, W. L. Colorimetric Estimation of Adrenalin.... 769
Seaton, S. G., H. L. Trumbull and H. Durham. Control Experiments in Chloropicrin Manufacture. II—Active Chlorine in the Sludge from the Manufacture of Chloropicrin.... 1068
  H. L. Trumbull, G. T. Sohl and W. I. Burt. Control Experiments in Chloropicrin Manufacture. I—The Effect of Varying Quantities of Lime upon the Yield of Chloropicrin.... 1068
Segerblom, W. Fire Caused by Yellow Phosphorus.... 297
  W. A. Hamor, L. C. Newell and A. M. Patterson. Chemical Reading Courses. (*See* McClelland, 1026)....701, 806
Segnitz, P. H. Note on the Catalysis of Permanganate Titrations... 1196
Selvig, W. A. and B. B. Kaplan. Hygroscopicity of By-Product Coke.... 783
Semon, W. L. and F. H. Heath. Reaction between Selenium Monochloride and Ethylene.... 1100
Shakespear, G. A. Automatic Methods of Gas Analysis Depending upon Thermal Conductivity. (*See* Weaver, *et al.*, 359).... 1027
Shaw, J. A. Method for the Determination of Thiocyanates in Ammoniacal Liquor and Waste Liquor from Ammonia Stills in the By-Product Coking Industry.... 676
Shaw, R. H. Studies on Technical Casein. III—Methods of Analysis.... 1168
Sheppard, S. E. New Turbidimeter for Solutions of Gelatin, Cellulose, and Varnishes.... 167
  S. S. Sweet and J. W. Scott, Jr. Jelly Strength of Gelatins and Glues, 1007; Correction.... 1214
Sherrard, E. C. and G. W. Blanco. Acid Hydrolysis of Sugar-Cane Fiber and Cottonseed Hulls.... 1160
Sherrick, J. L. Oil-Field Emulsions.... 133
Shreve, R. N. Dye Section, A. C. S., 298; Report of the Dye Division of the A. C. S.... 609
Silverman, A. Francis C. Phillips. Obituary.... 399
  New Illuminator for Microscopes—III.... 1200
Skinner, W. W. and W. F. Baughman. Determination of Iodide and Bromide in Mineral Waters and Brines.... 358
Smith, C. R. Determination of the Jellying Power of Gelatins and Glues by the Polariscope.... 878
Smith, G. F. and E. D. Campbell. Comparison of Accuracy in Analysis of Metallurgical Materials during the Past Twenty-Five Years.... 1020
Smith, W. B. Kreis Reaction of Cottonseed-Oil Products.... 764
Sohl, G. T., H. L. Trumbull, W. I. Burt and S. G. Seaton. Control Experiments in Chloropicrin Manufacture. I—The Effect of Varying Quantities of Lime upon the Yield of Chloropicrin.... 1068
Speakman, H. B. Seed-Culture Methods in the Production of Acetone and Butyl Alcohol by a Fermentation Process.... 581
Spear, E. B. Les Colloides Métalliques. Propriétés et Préparations, by Bary. (Book Review).... 1141
Spencer, G. C. Potash from Kelp. II—The Experimental Distillation of Kelp at Low Temperatures.... 682
  Potash from Kelp. III—The Preliminary Examination of Kelp Distillates.... 786
Spencer, G. L. Preservation of Bagasse in Sugar-Cane Mill Control. 1197
Stark, D. D. and E. W. Dean. Convenient Method for the Determination of Water in Petroleum and Other Organic Emulsions. 486
Steele, L. L. and F. M. Washburn. New Hexabromide Method for Linseed Oil.... 52
Stericker, W. Composition of Water-Glass Solutions.... 1026
Sterne, E. T. and L. F. Goodwin. Losses Incurred in the Preparation of Acetone by the Distillation of Acetate of Lime.... 240
Stieglitz, J. The Society's President for 1920. W. A. Noyes.... 106
Stoddard, W. B. and H. B. Faber. Short Commercial Analytical Methods for the Determination of Purity of Important Chemicals Used in Pyrotechnics.... 576
Sutherland, L. T. Chemical Warfare Post of the American Legion. 924
Sweet, S. S., S. E. Sheppard and J. W. Scott, Jr. Jelly Strength of Gelatins and Glues, 1007; Correction.... 1214
Swift, C. K. and P. A. Houseman. Preparation of Hematoxylin... 173

TABER, G. H. Some Notes on the Baumé Hydrometer.... 593
Talbot, H. P. The Chemists' Year Book, 1918–1919. *Edited* by Atack and Whinyates. (Book Review).... 101
  Relation of Educational Institutions to the Industries. Address, Chicago Meeting, A. C. S.... 943
Tanner, F. W. and B. Feuer. Action of Ultraviolet Light on the Yeast-Like Fungi—I.... 740
Taylor, F. O. Practical Standardization of Chemical Assay of Organic Drugs and Galenicals, by Lyons. (Book Review).... 1141
Taylor, G. F. Some Improvements on the Needle Type Thermocouple for Low Temperature Work.... 797
Taylor, M. C. and W. M. Dehn. Chemical Method for the Detection in Fruit of a Prior Frozen Condition.... 977
Teague, M. C. Determination of Carbon Monoxide in Air Contaminated with Motor Exhaust Gas.... 964
Teeters, W. R. Advanced Work for High School Chemistry Teachers.... 198
Thieme, C. O. Hardening Effects of Various Elements upon Lead.. 446
Thiessen, R. and G. St. J. Perrott. Carbon Black—Its Properties and Uses.... 324
Thomas, A. W. Review of the Literature of Emulsions.... 177
  and A. Frieden. Determination of Hydrochloric Acid and Neutral Chlorides in Leather.... 1186
Thompson, T. G. and J. H. Black. Intersolubility of Chloropicrin and Water.... 1066
  and F. J. Kopp. Pressures Produced by the Action of Sulfur Monochloride upon β,β'-Dichloroethyl Sulfide.... 1056
  and H. Odeen. Solubility of β,β'-Dichloroethyl Sulfide in Petroleum Hydrocarbons and Its Purification by Extraction with These Solvents.... 1057
Thurston, A. N. and J. S. McCune. Preservatives for Fermentable Beverage Samples.... 689
Tingle, A. Indexing References.... 909
  and A. M. Macmillan. Acidimetry of Red Wines and Fruit Juices.... 274
Tour, R. S. Direct Synthetic Ammonia Process.... 844
Trumbull, H. L., S. G. Seaton and H. Durham. Control Experiments in Chloropicrin Manufacture. II—Active Chlorine in the Sludge from the Manufacture of Chloropicrin.... 1068
  G. T. Sohl, W. I. Burt and S. G. Seaton. Control Experiments in Chloropicrin Manufacture. I—The Effect of Varying Quantities of Lime upon the Yield of Chloropicrin.... 1068
Tsujimoto, M. Occurrence of Squalene in the Egg Oil from Shark.. 73
  Squalene: A Highly Unsaturated Hydrocarbon in Shark Liver Oil, 63; Correction.... 395
Tunison, B. R. Future of Industrial Alcohols.... 370
Turley, T. B. and W. H. Waggaman. Production of Phosphoric Acid by Smelting Phosphate Rock in a Fuel-Fed Furnace.... 646

UYEDA, Y. Proximate Compositions of Korean Hemp and Ramie. 573

VEITCH, F. P. and T. D. Jarrell. Determination of the Water Resistance of Fabrics.... 26
  and B. S. Levine. Testing the Mildew Resistance of Textiles.... 139

WAGGAMAN, W. H. and T. B. Turley. Production of Phosphoric Acid by Smelting Phosphate Rock in a Fuel-Fed Furnace.... 646
Walczak, M. R. and H. I. Rice. Extraction of Bitumens from Mineral Aggregate.... 738
Walbott, S. Simple Alcohol-Testing Device.... 690
Walker, W. H. Division of Industrial Coöperation and Research of the Massachusetts Institute of Technology.... 394
Washburn, F. M. Constant Temperature Still Head for Light Oil Fractionation.... 73
  and L. L. Steele. New Hexabromide Method for Linseed Oil.... 52
Waters, C. E. New Method for the Determination of Sulfur in Oils, 482; Note.... 612
Weaver, E. R. Generation of Hydrogen by the Reaction between Ferrosilicon and a Solution of Sodium Hydroxide.... 232
  and P. G. Ledig. New Forms of Combustion Apparatus for Use in Gas Analysis.... 368
  and P. E. Palmer. Application of the Thermal Conductivity Method to the Automatic Analysis of Complex Mixtures of Gases. 894
  P. E. Palmer, H. W. Frantz, P. G. Ledig and S. F. Pickering. Automatic Methods of Gas Analysis Depending upon Thermal Conductivity. (*See* Shakespear, 1027).... 359
Weimar, A. C., W. M. Clark, H. F. Zoller and A. O. Dahlberg. Studies on Technical Casein. II—Grain-Curd Casein.... 1163
Weiss, J. M. and C. R. Downs. Catalytic Oxidation. I—Benzene. 228
Wesson, D. Les Amandes et l'Huile de Palme, by Baillaud and Stieltjes. (Book Review).... 413
West, C. J. Chemical and Engineering Laboratories.... 295
  Outlook for Research and Invention, by Hopkins. (Book Review). 412
Westman, L. E. Convention of Canadian Chemists.... 706
Wheeler, H. J. Mining and Manufacture of Fertilizing Materials and Their Relation to Soils, by Lloyd. (Book Review).... 517
Wherry, E. T. and J. A. Ambler. Naphthalene Sulfonic Acids. II—A Method for the Qualitative Detection of Some of the Naphthalene Sulfonic Acids.... 1085
Whitaker, M. C. Personalities. Perkin Medal Award.... 183
White, A. H. Manual of Industrial Chemistry, *Edited* by Rogers, *et al.* (Book Review).... 725
Whiting, A. L., T. E. Richmond and W. R. Schoonover. Determination of Nitrates in Soil.... 982
Whitney, W. R. Presentation Address. Willard Gibbs Medal Award.... 697
  The Littlest Things in Chemistry. Address of Acceptance. Chandler Medal Award.... 599
Williams, R. S. A Metallographic Study on Tungsten Steels, by Hultgren. (Book Review).... 1226
Wilson, J. A. Mechanism of Bating.... 1087
  and E. J. Kern. Nature of the Hide-Tannin Compound and Its Bearing upon Tannin Analysis.... 1149
  True Tanning Value of Vegetable Tanning Materials.... 465
Wilson, R. E. Soda Lime as an Absorbent for Industrial Purposes.. 1000
Wilson, T. E. Value of Technical Training in the Reconstruction of Industries. Address, Chicago Meeting, A. C. S.... 941
Winner, G. B. and G. H. Buchanan. Solubility of Mono- and Diammonium Phosphate.... 448
Winter, O. B. and C. S. Robinson. Electrometric Analysis of Arsenicals.... 775
Withrow, J. R. and J. M. Ort. Sugar Sirup from Home-Grown Sugar Beets.... 154
Witt, J. C. Laboratory Hood.... 596
  Rapid Preparation of Tables.... 591
Woodbridge, R. G., Jr. Nitrocellulose from Wood Pulp.... 380
Woodman, A. G. Standard Methods for the Examination of Water and Sewage. (Book Review).... 1037
Worischek, A. Photobibliographic Research Methods—The Compilation of Technical Data with the Aid of Photography.... 679

YORK, E. M. Purified Cresol (Cresylic Acid). (*See* Hamilton, 50). 296

ZDANOWICH, J. O. Cellulose Acetates.... 1173
Zerban, F. W. Relative Importance of Some Coloring Matters in Cane Juices and Sirups.... 744
Zoller, H. F. Studies on Technical Casein. IV—Standardization of the Borax Solubility Test for Commercial Caseins.... 1171
  W. M. Clark, A. O. Dahlberg and A. C. Weimar. Studies on Technical Casein. II—Grain-Curd Casein.... 1163

SUBJECT INDEX

THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY
VOLUME XII—1920

- ABRASIVE Materials in 1918. Katz. Gov. Pub ... 1220
- Absorbent, Soda-Lime as an—for Industrial Purposes. R. E. Wilson. 1000
- Accelerators, Action of Certain Organic—in Vulcanization of Rubber. G. D. Kratz, A. H Flower and C. Coolidge ... 317
- Accelerators, Effect of Certain—upon Properties of Vulcanized Rubber—II. G. D. Kratz and A. H. Flower ... 971
- Accelerators, Reactions of—during Vulcanization. C. W. Bedford and W. Scott ... 31
- Accident, Fatal Laboratory. Note ... 89
- Accident Prevention in Mines, Butte, Montana. Gov. Pub....722, 931
- Accidents. (*See* Works and Laboratory Accidents)
- Accidents at Metallurgical Works in U. S., 1918. Fay. Gov. Pub.. 513
- Accidents, Coke-Oven, in U. S., 1919. Adams. Gov. Pub ... 1121
- Accidents, Industrial, and Their Prevention. Ray. Gov. Pub ... 723
- Accidents, Metal-Mine, in U. S., 1918. Fay. Gov. Pub ... 513
- Accounting, Cost-, Value of—in Commercial Laboratories. W. W. Caswell ... 79
- Accounting, Metal-Mine. Holmes. Gov. Pub ... 513
- Accumulators, Nickel-Iron. Note ... 182
- Acetates, Cellulose. J. O. Zdanowich ... 1173
- Acetic Acid, Determination of—in Pyroligneous Acid. V. E. Grotlisch ... 1183
- Acetic Acid, Modification of Thompson Method for Determination of—in White Lead. L. McMaster and A. E. Goldstein ... 170
- Acetic Acid, New Method for Determination of—in Acetates. O. A. Pickett ... 570
- Acetone and Butyl Alcohol, Seed-Culture Methods in Production of—by a Fermentation Process. H. B. Speakman ... 581
- Acetone, Losses Incurred in Preparation of—by Distillation of Acetate of Lime. L. F. Goodwin and E. T. Sterne ... 240
- Acetylene Flame, Distribution of Energy in Spectrum of. Coblentz. Gov. Pub ... 408
- Acid, Indicators Used for Determining Free—in Pickling Solutions. C. L. Boyle ... 571
- Acid Sludge, Utilization of Asphaltic Base—Obtained in Refining Petroleum and Shale Oils. C. Baskerville ... 30
- Acid Soils, Investigation of—by Means of Hydrogen Electrode. Acidity and Acidimetry of Soils—II. H. G. Knight ... 457
- Acidity and Acidimetry of Soils. (*See* Soils: Acidity and Acidimetry)
- Acids:
  - Acetic, Determination of—in Pyroligneous Acid. V. E. Grotlisch. 1183
  - Acetic, New Method for Determination of—in Acetates. O. A. Pickett ... 570
  - Battery, Nitrates and Nitrites in. Sefton. Gov. Pub ... 513
  - Benzoic, Purification of—by Fractional Condensation. M. Phillips and H. D. Gibbs ... 277
  - Chromic, Continuous Process for Electrolytic Regeneration of. R. H. McKee and S. T. Leo ... 16
  - Cresylic (Purified Cresol). H. C. Hamilton ... 50
  - Fatty, Detection of Oils other than Linseed in Paints by Means of Hexabromide Number of. H. S. Bailey and W. D. Baldsiefen.. 1189
  - Fatty, Heat Balance of Distillation Plant for Recovery of—from Cottonseed Foots. J. Alsberg ... 490
  - Hydrochloric, Production of—from Chlorine and Water. H. D. Gibbs ... 538
  - Naphthalene Sulfonic. (*See* Naphthalene Sulfonic Acids)
  - Nitric, Absorption of Oxides of Nitrogen by. E. K. Rideal ... 531
  - Phosphoric, Production of—by Smelting Phosphate Rock in Fuel-Fed Furnace. W. H. Waggaman and T. B. Turley ... 646
  - Sulfuric and Nitric, Freezing Points of Mixtures of. W. C. Holmes. 781
  - Sulfuric, Commercial, Rapid Method for Quantitative Determination of Arsenic in. A. A. Kohr ... 580
  - Sulfuric, Manufacture of. Note ... 181
  - Sulfuric, Manufacture of—in U. S. Wells and Fogg. Gov. Pub.. 1221
  - Tariff Act of 1913 concerning Boric, Citric, Formic, Gallic, Pyrogallic, Lactic, Oxalic, Tannic, and Tartaric Acids. Gov. Pub... 406
- ADDRESSES AND CONTRIBUTED ARTICLES ... 79, 177, 290, 370, 597, 690, 801, 909, 1015, 1122, 1202
- Adrenalin, Colorimetric Estimation of. W. L. Scoville ... 769
- Aëronautics: Inflammability of Jets of Hydrogen and Inert Gas. P. G. Ledig ... 1098
- Aircraft-Engine Fuels, New Process for. Paris and Paris, Jr. Gov. Pub ... 303
- Aircraft Engines, Altitude Laboratory for Testing of. Dickinson and Boutell. Gov. Pub ... 303
- Aircraft Engines, Power Characteristics of Fuels for. Gov. Pub... 406
- Airplane Dopes and Doping. Smith. Gov. Pub ... 96
- Airplane Fabric, Cotton. Taylor and Earle. Gov. Pub ... 1221
- Airplane Tensiometer. Larson. Gov. Pub ... 96
- Airplane Woods, Moisture Resistant Finishes for. Dunlap. Gov. Pub ... 930
- Alaskan Mining Industry in 1918. Martin. Gov. Pub ... 96
- ALCOHOLS:
  - *A. C. S. News Service:*
    - Wood, Explains Danger of. (*See* Editorial, 109) ... 197
  - *Addresses and Original Papers:*
    - Butyl—As Medium for Determination of Saponification Numbers. A. M. Pardee, R. L. Hasche and E. E. Reid ... 481
    - Future of Industrial Alcohols. B. R. Tunison ... 370
    - Simple—Testing Device. S. Waldbott ... 690
    - Sugar-Cane Fiber and Cottonseed Hulls, Acid Hydrolysis of. E. C. Sherrard and G. W. Blanco ... 1160
    - Vapor Composition of—Water Mixtures. W. K. Lewis ... 496
    - Wood—Coöperative Caution. C. Baskerville ... 81
  - *Editorials:*
    - Evolution in Alcohol Administration ... 1044
    - For Industrial and Scientific Purposes. Note ... 524
    - One-Sided Greasing ... 626
    - Prophetic ... 731
    - Safety in Speech. (*See* A. C. S. News Service Bulletin, 197)... 109
  - *Government Publications:*
    - Comparative Fuel Values of Gasoline and—in Internal Combustion Engines ... 823
    - Denatured Alcohol ... 723
- Alfalfa, Brown and Black, Losses of Organic Matter in Making. Swanson, *et al.* Gov. Pub ... 308
- Alien Property Custodian: Crippling a Great Work. Editorial... 835
  - Lying Down on the Job. Editorial. (*See* Franklin., 1132) ... 1042
- Alkali Fusions:
  - I—Fusion of Sodium *p*-Cymene Sulfonate with Sodium Hydroxide for Production of Carvacrol. H. D. Gibbs and M. Phillips. (*See* Hixson and McKee, 296) ... 145
  - II—Fusion of Sodium Benzene *m*-Disulfonate with Sodium Hydroxide for Production of Resorcinol. M. Phillips and H. D. Gibbs, 857; Correction ... 1028
- Allied Chemical and Dye Corporation. Note ... 1132
- Alloys:
  - Aluminium—Castings, Blowholes, Porosity, and Unsoundness in. Anderson. Gov. Pub ... 619
  - Analysis of Molybdenum, Cobalt, and Chromium Alloys. J. R. Camp and J. W. Marden ... 998
  - Light Aluminium Casting, Effect of Heat Treatment. Merica and Karr. Gov. Pub ... 99
  - Light Aluminium Casting, Rapid and Systematic Method for Analysis of. R. M. Berry ... 998
- Aluminium:
  - Alloys of—and Magnesium with Copper, Nickel and Manganese. Merica, *et al.* Gov. Pub ... 99
  - Aluminium and Bauxite. Hill. Gov. Pub. 1918, 512; 1919 ... 1033
  - Casting Alloys, Light, Effect of Heat Treatment on. Merica and Karr. Gov. Pub ... 99
  - Casting Alloys, Light, Rapid and Systematic Method for Analysis of. R. M. Berry ... 998
  - Determination of—in Flake or Dust, in Pyrotechnics. H. B. Faber and W. B. Stoddard ... 576
  - Dross, Evaluation of. F. K. Bezzenberger ... 78
  - In Norway. Note ... 83
  - Light Alloys. Merica. Gov. Pub ... 96
  - Reflective Properties of Alloys with Magnesium and Zinc. Waltenberg and Coblentz. Gov. Pub ... 409
- Alundum Filtering Crucibles, Note on Use of. D. T. Englis ... 799
- AMERICAN CERAMIC SOCIETY:
  - Joint Meeting with British Society of Glass Technology, Pittsburgh, Pa., September 1, 1920 ... 924
- AMERICAN CHEMICAL SOCIETY:
  - William Albert Noyes, Society's President for 1920. J. Stieglitz.. 106
  - *59th Meeting,* St. Louis, Mo., April 12 to 16, 1920:
    - All Ready for the St. Louis Meeting. J. W. Harrington. A. C. S. News Service ... 395
    - Announcement ... 195
    - Divisions to the Front. Editorial ... 418
    - General Meeting ... 420
    - Matters of Business. Council Meeting ... 419
    - Program of Papers ... 500
    - Spring Meeting in St. Louis. Editorial ... 210
  - ADDRESSES:
    - Introductory Address. W. A. Noyes ... 423
    - Chemical Warfare. A. A. Fries ... 423
    - Victory and Its Responsibilities. C. H. Herty ... 429
  - SYMPOSIUM:
    - Ceramic Processes Associated with Colloid Phenomena. A. V. Bleininger ... 436
    - Some Practical Applications of Colloidal Chemistry. J. Alexander. (*See* page 612) ... 434
  - *60th (Annual) Meeting,* Chicago, Ill., September 6 to 10, 1920:
    - Cellulose Symposium for Chicago Meeting. G. J. Esselen, Jr... 814
    - Chicago Meeting. Editorial ... 730
    - Council Meeting ... 938
    - General Meeting ... 939
    - In the Alembic of Publicity. J. W. Harrington ... 705
    - Program of Papers ... 1022
    - Setting the Scenes for the Chicago Meeting. J. W. Harrington.. 918
  - *A. C. S. News Service:*
    - Bulletin. Explains Danger of Wood Alcohol. (*See* Editorial, Safety in Speech, 109) ... 197
    - Editorial ... 4
    - Report. J. W. Harrington ... 197
  - *Committees:*
    - Coöperation between Universities and Industries. Report. W. A. Noyes ... 439
    - Cottonseed Products. Report. T. C. Law ... 707
    - Endowment of A. C. S. Report. I. K. Phelps ... 442
    - Foreign Trade. National Foreign Trade Council Report. Note. 298
    - Guaranteed Reagents and Standard Apparatus. Drawings of Standard Apparatus. W. D. Collins ... 817
      - Report. W. D. Bigelow ... 439
    - Occupational Diseases in Chemical Trades. Report. C. Baskerville ... 439
    - Publication of Compendia of Chemical Literature, etc ... 195
    - Status of College Professors. Improvement of Conditions for College Instructing Staffs. W. McPherson ... 813
    - To Define Field Covered by Respective Divisions and Sections of A. C. S. Report. H. E. Howe ... 438
    - To Formulate Specifications for Construction of Polariscope for Laboratory Use. Report. W. D. Bigelow ... 442
    - Unit Weights for Purchase of Reagents. W. D. Collins ... 1206
  - *Divisions:*
    - Dye Division:
      - Announcement of St. Louis Meeting. R. N. Shreve ... 298
      - Report of St. Louis Meeting. R. N. Shreve ... 609

  Editorials:
    Caught Up...... 1147
    Editorial Note...... 315
    Help Wanted...... 522
    How Best to Serve...... 731
    Increase the Dues...... 834
    Mutual Obligations...... 836
    Publicity...... 4
    Safety in Speech. (*See* A. C. S. News Service Bulletin, 197)...... 109
    Substance Rather than Shadow. (*See* Editorial, 938)...... 1043
    Technical Monographs. Note...... 1044
  Secretary's Office:
    Advisory Committee Minutes. C. L. Parsons...... 84
    Bequest to the A. C. S...... 294
    Officers for 1920...... 2
  Sections:
    New York. Joint Meeting with Other Chemical Societies, New York City, October 15, 1920: Proposed New Departures in Government Chemical Work...... 1126
    Rochester. Note...... 197
AMERICAN DYES INSTITUTE:
  Report of Committee on Legislation, July 15, 1920...... 924
AMERICAN ELECTROCHEMICAL SOCIETY:
  37th General Meeting, Boston, Mass., April 8 to 10, 1920; Program of Papers, 397; Report. J. W. Richards...... 503
  38th Meeting, Cleveland, Ohio, September 30 to October 2, 1920. Report. J. W. Richards...... 1128
  New York Section, Joint Meeting, October 15, 1920...... 1126
AMERICAN INSTITUTE OF CHEMICAL ENGINEERS:
  12th Annual Meeting, Savannah, Ga., December 2 to 6, 1919. Report. J. C. Olsen...... 85
  Canada, June 28 to July 3, 1920. Report. J. C. Olsen...... 812
  Joint Meeting with Other Chemical Societies, New York City, October 15, 1920: Proposed New Departures in Government Chemical Work...... 1126
AMERICAN PHARMACEUTICAL ASSOCIATION:
  Scientific Section. Announcement of Annual Convention...... 397
American Progress in Bacteriological Sugars. E. H. Eitel...... 1202
American Society of Mechanical Engineers...... 1214
Ammonia:
  Ammonia-Free Water, Preparation of. G. C. Baker...... 798
  Commercial Oxidation of Ammonia. G. A. Perley......5, 119
  Direct Synthetic—Process. R. S. Tour...... 844
  Distillation of Ammonia. B. S. Davisson...... 176
  Industrial Synthetic Ammonia. Note...... 182
  Precipitation of Sulfur from Crude Mustard Gas by Means of Ammonia. W. A. Felsing and S. B. Arenson...... 1065
  Preparation of Nitrogen and Hydrogen Mixture by Decomposition of Ammonia. R. O. E. Davis and L. B. Olmstead...... 316
  Production of—and Formates from Cyanides, Ferrocyanides, and Cyanized Briquets. G. W. Heise and H. E. Foote...... 331
  Source of Nitrate of Ammonia. Note...... 390
  Synthesis, Electrically Heated Bomb for. R. O. E. Davis and H. Bryan...... 287
  Synthesis, Purification of Compressed Gases in Testing Catalysts for. R. O. E. Davis...... 289
  Synthetic Ammonia. Note...... 389
  Vapor Pressure of Ammonia. Cragoe, *et al.* Gov. Pub...... 619
Ammonium Acid Fluoride, Titration of. W. S. Chase...... 567
Ammonium Nitrate, Formaldehyde Method for Determining. J. T. Grissom...... 172
Ang-Khak, Chinese, Laboratory Experiments on Manufacture of—in U. S. M. B. Church...... 45
Anhinga. Note...... 390
Aniline and Ethyl Alcohol, Catalysts Which Promote Reaction between. T. B. Johnson, A. J. Hill and J. J. Donleavy...... 636
Aniline, Pure, Some Physical Constants of. C. L. Knowles...... 881
Annual Reports, London Chemical Society. E. J. Crane...... 1213
Anticlines near Maverick Springs, Wyoming. Collier. Gov. Pub...... 722
Antimony and Arsenic Compounds. Quantitative Studies in Chemotherapy, I. Voegtlin, *et al.* Gov. Pub...... 1138
Antimony in 1918. Ferguson. Gov. Pub...... 204
APPARATUS. (*See under name of piece*)
Apparatus and Instruments, Scientific. Gov. Pub...... 96
Apparatus, Duty-Free. Playing Their Game. Editorial...... 1146
Apparatus for Intermittent Testing. Vinal and Ritchie. Gov. Pub. 1139
Apparatus, Standard, Drawings of. W. D. Collins...... 817
Arc Lamp, New Cadmium-Vapor. Bates. Gov. Pub...... 619
Aromatic Compounds, Use of Catalysts in Sulfonation of. J. A. Ambler and W. J. Cotton...... 968
Arsenic. Hill. Gov. Pub., 304; 1919...... 1139
Arsenic and Antimony Compounds. Quantitative Studies in Chemotherapy, I. Voegtlin, *et al.* Gov. Pub...... 1138
Arsenic Compounds. Note...... 182
Arsenic, Detection of—in Sulfur. H. S. Davis and M. D. Davis...... 479
Arsenic, Rapid Method for Quantitative Determination of—in Commercial Sulfuric Acid. A. A. Kohr...... 580
Arsenic Trichloride, Preparation of—from White Arsenic and Phosgene. L. H. Milligan, W. A. Baude and H. G. Boyd...... 221
Arsenicals, Electrometric Analysis of. C. S. Robinson and O. B. Winter...... 775
Arsphenamine, Effect of Shaking—in Air. Roth. Gov. Pub...... 1138
Asbestos in 1918. Diller. Gov. Pub...... 512
Asphalt and Allied Substances, 1918. Osborn. Gov. Pub...... 618
Asphaltic Base Acid Sludge, Utilization of—Obtained in Refining Petroleum and Shale Oils. C. Baskerville...... 30
ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS:
  36th Annual Convention, Washington, D. C., November 17 to 19, 1919. C. L. Alsberg...... 86
ASSOCIATION OF SCIENTIFIC APPARATUS MAKERS OF THE UNITED STATES OF AMERICA:
  2nd Annual Meeting, Washington, D. C., April 22 and 23, 1920. 609
Atoms, Structure of—and Its Bearing on Chemical Valence. I. Langmuir...... 386

BACHARACH Bill. Editorials......107, 108, 315, 627, 1146
Bacteria, Iron-Depositing. Harder. Gov. Pub...... 98
Bacteria, Yeasts, and Spores, Modification of Howard Method for Counting—in Tomato Products. H. M. Miller...... 766
Bagasse, Paper-Making from. Note...... 83
Bagasse, Preservation of—in Sugar-Cane Mill Control. G. L. Spencer...... 1197
Balata and Gum Chicle, Question of Identity of. (*See* THIS JOURNAL, **11** (1919), 874) C. A. Browne...... 199
Balloon Fabrics, Testing. Edwards and Moore. Gov. Pub...... 96
Balloon Gas, Testing. Edwards. Gov. Pub...... 303
Barium Chemical and Lithopone Industries, 1919. Gov. Pub...... 1138
Barium Products and Barytes in 1918. Stose. Gov. Pub...... 930
Barley, Pearl: Manufacture and Composition. J. A. LeClerc and C. D. Garby...... 451
Bating, Mechanism of. J. A. Wilson...... 1087
Baumé Hydrometer, Notes on. G. H. Taber...... 593
Bauxite and Aluminium. Hill. Gov. Pub., 1918, 512; 1919...... 1033
Bead and Flame Tests, Substitutes for Platinum Wire in. C. C. Kiplinger...... 500
Beet-Sugar Factory Products, Determination of Moisture in. V. L. Aikin...... 979
Beet-Sugar Industry, Chemical Control in. S. J. Osborn...... 803
Beets, Sugar-, Sirup from Home-Grown. J. M. Ort and J. R. Withrow 154
Benzene. Catalytic Oxidation—I. J. M. Weiss and C. R. Downs.. 228
Benzene, Power Characteristics of 20 Per cent—Mixture. Roberts. Gov. Pub...... 406
Benzene, Sulfur in. Note...... 390
Benzoic Acid, Purification of—by Fractional Condensation. M. Phillips and H. D. Gibbs...... 277
Beverage Samples, Preservatives for Fermentable. J. S. McCune and A. N. Thurston...... 689
Beverages and Foods, Awards for Theses on. Note...... 716
Beverages, Cereal. Gov. Pub...... 96
Beverages, "Fake" Orange. Gov. Pub...... 1138
Biological Products, Regulation of—in England. Gov. Pub...... 823
Bismuth. Hill. Gov. Pub., 304; 1919...... 1139
Bitumens, Extraction of—from Mineral Aggregate. M. R. Walczak and H. I. Rice...... 738
Boerner Sampler, Modified. Boerner. Gov. Pub...... 1034
Bogert, M. T., Declines. Editorial...... 731
Bomb, Electrically Heated—for Ammonia Synthesis. R. O. E. Davis and H. Bryan...... 287
Bone-Black and Decolorizing Carbons. W. D. Horne...... 1015
Bookplate of Dr. Joseph Priestley. C. A. Browne...... 611
BOOK REVIEW (*See separate heading*)
Borax, Crop Injury by—in Fertilizers. Schreiner, *et al.* Gov. Pub.. 619
Borax Solubility Test, Standardization of—for Commercial Caseins. Studies on Technical Casein—IV. H. F. Zoller...... 1171
Boric Acid and Borax. Tariff Act of 1913. Gov. Pub...... 406
Boric Acid Modification of Kjeldahl Method for Crop and Soil Analysis. F. M. Scales and A. P. Harrison...... 350
Botulism from Eating Canned Ripe Olives. Armstrong, *et al.* Gov. Pub......406, 1032
Botulism. Protective Measures and Cautions. Gov. Pub...... 406
Brass, Corrosion of—in Dilute Electrolytes. J. H. Reedy and B. Feuer...... 541
Bricks, Clay Fire, Porosity and Volume Changes of—at Furnace Temperatures. Loomis. Gov. Pub...... 823
Brines and Mineral Waters, Determination of Iodide and Bromide in. W. F. Baughman and W. W. Skinner...... 358
British Import and Export of Chemicals. Note...... 83
British Nitrogen Products Committee Report...... 391
BRITISH SOCIETY OF GLASS TECHNOLOGY:
  Joint Meeting with American Ceramic Society, Pittsburgh, Pa., September 1, 1920...... 924
Bromide and Iodide, Determination of—in Mineral Waters and Brines. W. F. Baughman and W. W. Skinner...... 358
Bromine, Salt, and Calcium Chloride in 1918. Stone. Gov. Pub... 98
Bulb, Effective Connecting. C. M. Clark...... 366
Bureau of Census. Gov. Pub......98, 407
Bureau of Chemistry, Report of Chemist, 1919. Gov. Pub...... 409
Bureau of Fisheries. Gov. Pub...... 98
Bureau of Internal Revenue. Gov. Pub...... 407
Bureau of Mines: Director's Annual Report. Gov. Pub...... 307
  Dr. Manning Retires. Editorial...... 524
  Experiment Stations. Manning. Gov. Pub...... 307
  Government Publications......98, 307, 407, 513, 618, 722, 823, 931, 1033, 1139, 1221
  New Experiment Station. Note...... 1028
Bureau of Standards:
  Conservation of Standard Samples of. Note...... 717
  Director's Annual Report. Gov. Pub...... 308
  Government Publications......99, 205, 307, 408, 513, 619, 723, 823, 931, 1033, 1139, 1221
Burns, Acid, on Hands of Solderers. Keatley. Gov. Pub...... 1138
Butter and Allied Products, Volumetric Method for Estimation of Neutralizers in. L. W. Ferris...... 757
Butyl Alcohol and Acetone, Seed-Culture Methods in Production of—by Fermentation Process. H. B. Speakman...... 581
Butyl Alcohol as Medium for Determination of Saponification Numbers. A. M. Pardee, R. L. Hasche and E. E. Reid...... 481
By-Product Coking Industry, Determination of Thiocyanates in Ammoniacal Liquor and Waste Liquor in. J. A. Shaw...... 676

Book Reviews......101, 309, 412, 516, 725, 827, 1035, 1141, 1223
Amandes et l'Huile de Palme, by Baillaud and Stieltjes. D. Wesson.. 413
Analysis of Babbitt, by Brakes. W. A. Cowan...... 413
Animal Fats and Oils, by Andés. A. Campbell...... 1223
Annual Reports of the Society of Chemical Industry on the Progress of Applied Chemistry. Issued by the Society of Chemical Industry. W. A. Hamor...... 1036
Boiler Feed Water, by Jackson. F. J. Pond...... 829
Catalysis in Industrial Chemistry, by Henderson. J. Johnston...... 101
Chemical Calculation Tables, by Wells. J. C. Olsen...... 516
Chemistry for Textile Students, by North and Bland. E. C. Bertolet. 1224
Chemists' Year Book, 1918–1919, by Atack and Whinyates. H. P. Talbot...... 101
Colloidal Chemistry and Its General and Industrial Applications, 1918. Second Report. H. N. Holmes...... 101
Colloides Métalliques. Propriétés et Préparations, by Bary. E. B. Spear...... 1141
Colloids in Biology and Medicine, by Bechhold, and *translated* by Bullowa. W. D. Bancroft...... 412
Commercial Laboratory Notes, by Petty. H. Fay...... 309
Condensed Chemical Dictionary. *Compiled* and *edited* by Turner, *et al.* A. M. Patterson......102, 725
Creative Chemistry, by Slosson. H. E. Howe...... 516
Dyeing with Coal-Tar Dyestuffs, by Whittaker. L. A. Olney...... 309
Explosives, by Barnett. A. M. Comey...... 1035
Farmaceutiche e Industrie Chimiche, Annuario per le. Anno I, 1918, by Nasini, *et al.* W. Haynes...... 413
Food Inspection and Analysis, by Leach and Winton. C. A. Browne. 828
From Newton to Einstein, by Harrow. J. M. Mathews...... 725

Hydrogenation of Oils, by Ellis. P. C. McIlhiney.... 309
Liquid Fuel for Internal Combustion Engines, by Moore. S. W. Parr.... 309
Making, Shaping, and Treating of Steel, by Camp and Francis. D. J. Demorest.... 1226
Manual of Cyanidation, by Hamilton. J. V. N. Dorr.... 829
Manual of Industrial Chemistry, *edited* by Rogers, *et al.* A. H. White. 725
Metallographic Study on Tungsten Steels, by Hultgren. R. S. Williams.... 1226
Metallography. Part I, Principles of Metallography, by Hoyt. H. Fay.... 828
Military Pyrotechnics, by Faber. H. R. Moody.... 828
Millions from Waste, by Talbot. W. H. Dickerson.... 827
Mining and Manufacture of Fertilizing Materials and Their Relation to Soils, by Lloyd. H. J. Wheeler.... 517
Modern Pulp and Paper Making, by Witham. T. J. Keenan.... 1224
Organization of Industrial Scientific Research, by Mees. P. G. Nutting.... 1037
Outlook for Research and Invention, by Hopkins. C. J. West.... 412
Petroleum Handbook, by Andros. G. W. Gray.... 516
Practical Standardization of Chemical Assay of Organic Drugs and Galenicals, by Lyons. F. O. Taylor.... 1141
Profession of Chemistry, by Pilcher. E. O'Neill.... 1035
Standard Methods for Examination of Water and Sewage. A. G. Woodman.... 1037
Standards and Tests for Reagent Chemicals, by Murray. W. D. Collins.... 1035
Technical Handbook of Oils, Fats, and Waxes. Vol. II—Practical and Analytical, by Fryer and Weston. W. D. Richardson.... 516
Treatise on General and Industrial Inorganic Chemistry, by Molinari, and *translated* by Pope. W. McPherson.... 1036
White Lead: Its Use in Paint, by Sabin. H. A. Gardner.... 517
Yeasts, by Guilliermond. H. T. Graber.... 1225

CADMIUM Electrode for Storage Battery Testing. Holler and Braham. Gov. Pub.... 308
Cadmium in 1919. Siebenthal. Gov. Pub.... 931
Cadmium-Vapor Arc Lamp, New. Bates. Gov. Pub.... 619
Calcium Acetate: Losses Incurred in Preparation of Acetone by Distillation of Acetate of Lime. L. F. Goodwin and E. T. Sterne.... 240
Calcium and Magnesium Carbonates. Conner and Noyes. Gov. Pub.... 308
Calcium and Potassium Sulfates, Formation of Double Salts of—at 100° C. E. Anderson and R. J. Nestell.... 243
Calcium Chloride, Salt, and Bromine in 1918. Stone. Gov. Pub.... 98
Calcium: McCrudden Gravimetric Method Modified. J. O. Halverson and J. A. Schulz.... 77
Calcium Sulfate, Effect on Soil Solubility. McCool and Millar. Gov. Pub.... 723
Calendar of Meetings.... 87, 197, 299, 398, 505, 611, 712, 815, 924, 1129, 1214
California Institute of Technology. Note.... 395
Camphor. Editorial Note.... 524
Camphor, Synthetic. Editorial Note.... 628
Camphor Trees, Machine for Trimming. Russell. Gov. Pub.... 619
Canadian Chemists, Convention of. L. E. Westman.... 706
Carbon Black: Its Properties and Uses. G. St. J. Perrott and R. Thiessen.... 324
Carbon Dioxide Content, Relationship of Hydrogen-Ion Concentration of Natural Waters to. R. E. Greenfield and G. C. Baker, 989; Correction.... 1214
Carbon Dioxide, Indicators for—in Air and Flue Gas. Milligan, *et al.* Gov. Pub.... 931
Carbon, Electrolytic Resistance Method for Determining—in Steel. Cain and Maxwell. Gov. Pub.... 308
Carbon Monoxide, Determination of—in Air Contaminated with Motor Exhaust Gas. M. C. Teague.... 964
Carbon Monoxide, Removal of—from Air. A. B. Lamb, W. C. Bray and J. C. W. Frazer.... 213
Carbonate and Silicate Rocks, Analysis of. Hillebrand. Gov. Pub.... 305, 407
Carbons, Decolorizing, and Bone-Black. W. D. Horne.... 1015
Carvacrol, Fusion of Sodium *p*-Cymene Sulfonate with Sodium Hydroxide for Production of. Alkali Fusions—I. H. D. Gibbs and M. Phillips. (*See* Hixson and McKee, 296).... 145
Casein, Influence of Method of Manufacture on Use of—in Glue Making. S. Butterman.... 141
Casein, Technical, Studies on:
  I—Introduction. W. M. Clark.... 1162
  II—Grain-Curd Casein. W. M. Clark, H. F. Zoller, A. O. Dahlberg and A. C. Weimar.... 1163
  III—Methods of Analysis. R. H. Shaw.... 1168
  IV—Standardization of the Borax Solubility Test for Commercial Caseins. H. F. Zoller.... 1171
Castor-Oil Industry. Shrader. Gov. Pub.... 1139
Catalog, International, of Scientific Literature, 1919. Gov. Pub.... 406
Catalysis:
  Catalytic Oxidation. I—Benzene. J. M. Weiss and C. R. Downs. 228
  In Manufacture of Ether. H. Schlatter.... 1101
  Of Permanganate Titrations. P. H. Segnitz.... 1196
  Of Reaction between Aniline and Ethyl Alcohol. T. B. Johnson, A. J. Hill and J. J. Donleavy.... 636
  In Sulfonation of Aromatic Compounds. J. A. Ambler and W. J. Cotton.... 968
Celluloid Industry, Japanese. Note.... 182
Cellulose:
  Acetate, Certain Aspects of Chemistry of—from Colloidal Viewpoint. G. J. Esselen, Jr.... 801
  Acetates. J. O. Zdanowich.... 1173
  Determination of—in Rubber Goods. Epstein and Moore. Gov. Pub.... 513
  Determination of—in Woods. W. H. Dore, 264; Correction.... 395
  Determination of—in Woods. S. A. Mahood.... 873
  New Turbidimeter for Solutions of—, Gelatin, and Varnishes. S. E. Sheppard.... 167
  Phthalate. H. A. Levey.... 743
Cement in 1918. Burchard. Gov. Pub.... 618
Cements for Spark-Plug Electrodes. Staley. Gov. Pub.... 513
Ceramic Insulators for Spark Plugs. Gov. Pub.... 304
Ceramic Processes Associated with Colloid Phenomena. A. V. Bleininger.... 436
Cereal Beverages. Congressional Committee Hearings. Gov. Pub.. 96
Cereal Products, Simple Method for Measuring Acidity of—. Application to Sulfured and Unsulfured Oats. Birckner. Gov. Pub.... 308
Cereals, Moisture Content of. O. A. Nelson and G. A. Hulett.... 40
Chandler Lecture:
  Note.... 395
  Introductory Remarks. R. H. McKee.... 599
  Acceptance Address. Littliest Things in Chemistry. W. R. Whitney.... 599
  Presentation Address. C. F. Chandler.... 607
Chapin Report. Editorial. (*See* Chapin, 1130).... 1042
Charcoal, Use of—in Determining Gasoline Content of Natural Gas. Gasoline from Natural Gas—II. R. P. Anderson and C. E. Hinckley. (*See* Anderson, 547).... 735
Chemical and Engineering Laboratories. Bibliography. C. J. West. 295
Chemical Conference, International. C. Lormand.... 925
Chemical Foundation, Inc., Meeting of Stockholders, December 2, 1919. 87
  Patents. R. Hoguet.... 297
Chemical Industries and Trade of Norway. O. P. Hopkins.... 632
Chemical Industries, President-Elect Harding's Views. Editorial.... 1146
Chemical Industries, Reconstruction Aspects of Some—in U. S. E. Gudeman.... 376
Chemical Industries, Sixth National Exposition of. (*See* Exposition)
Chemical Industry and Trade of Italy. O. P. Hopkins.... 525
Chemical Industry and Trade of Japan. O. P. Hopkins.... 110
Chemical Industry and Trade of Spain. O. P. Hopkins.... 223, 298
Chemical Industry and Trade of Sweden. O. P. Hopkins.... 1045
Chemical Industry, French, Growth of. Note.... 181
Chemical Industry, Italian, Impressions of. C. L. Parsons.... 907
Chemical Laboratories, Dartmouth and Yale. Editorial Note.... 1044
Chemical Market in India. H. S. Bennett.... 395
Chemical Preparedness. C. A. Lyford.... 506
Chemical Reading Courses. W. A. Hamor, L. C. Newell, A. M. Patterson and W. Segerblom. (*See* McClelland, 1026).... 701, 806
Chemical Reagents, Some American-Made. W. D. Collins.... 800
Chemical Societies in New York City. Program for 1920–1921 Season.... 1025
Chemical Societies. Rope Making. Editorial, 626; Editorial Note. 732
  Machinery Installed—Lubrication Next. Editorial.... 1147
Chemical Society, London, Annual Reports. E. J. Crane.... 1213
Chemical Warfare Post of American Legion:
  Meeting, New York, N. Y., September 22, 1920. Announcement.. 924
  Reorganization.... 961
Chemical Warfare Service:
  Editorials.... 2, 107, 314, 627, 730
Chemical Warfare Service, U. S. A., Contributions from... 213, 1054
Chemical Work, Government, Proposed New Departures in.... 1126
Chemicals, British Import and Export of. Note.... 83
Chemicals, Our Foreign Trade in. O. P. Hopkins.... 840
Chemist, College Trained, Examination of—for Government Service. M. L. Hamlin. (*See* Cotton, This Journal, **11** (1919), 1142).... 89
Chemist, Research, Education of. R. E. Rose.... 947
Chemist, Responsibilities of the—as a Citizen. H. W. Jordan... 629
Chemistry, Littlest Things in. Chandler Medal Acceptance Address. W. R. Whitney.... 599
Chemistry's Contribution to Life Sciences. Address, Chicago Meeting, A. C. S. A. S. Loevenhart.... 1122
Chemists' Club:
  Annual Meeting, New York, May 5, 1920. Report.... 610
  Editorial Note.... 732
Chemists, Organic, Qualifications of. M. L. Crossley.... 951
Chemists, Study of Economic Status of—in Government Service, 10 Educational Institutions and 37 Firms. L. F. Kebler.... 1206
Chemotherapy, Quantitative Studies in. I—Arsenic and Antimony Compounds. Voegtlin, *et al.* Gov. Pub.... 1138
Chlorides, Effect of—on Nitrometer Determination of Nitrates. M. T. Sanders.... 169
Chlorides: Equilibria in Solutions Containing Mixtures of Salts—II. W. C. Blasdale.... 164
Chlorides, Neutral, and Hydrochloric Acid, Determination of—in Leather. A. W. Thomas and A. Frieden.... 1186
Chlorine, Active, in Sludge from Manufacture of Chloropicrin. Control Experiments in Chloropicrin Manufacture—II. H. L. Trumbull, S. G. Seaton and H. Durham.... 1068
Chlorine and Influenza. C. Baskerville.... 293
Chlorine as a Preventive of Influenza. H. Hale.... 806
Chlorine, Production of Hydrochloric Acid from—and Water. H. D. Gibbs.... 538
Chlorine-Treated Water, Studies on Corrosive Action of. I—Effects of Steel on Equilibrium: $Cl_2 + H_2O \rightleftarrows HCl + HClO$, and of Products of Equilibrium on Steel. G. L. Clark and R. B. Iseley... 1116
Chloropicrin and Water, Intersolubility of. T. G. Thompson and J. H. Black.... 1066
Chloropicrin Manufacture, Control Experiments in:
  I—Effect of Varying Quantities of Lime upon Yield of Chloropicrin. H. L. Trumbull, G. T. Sohl, W. I. Burt and S. G. Seaton. 1068
  II—Active Chlorine in Sludge from Manufacture of Chloropicrin. H. L. Trumbull, S. G. Seaton and H. Durham.... 1068
Chromic Acid, Continuous Process for Electrolytic Regeneration of. R. H. McKee and S. T. Leo.... 16
Chromite in 1918. Diller. Gov. Pub.... 722
Chromite of Kenai Peninsula, Alaska. Gill. Gov. Pub.... 512
Chromium, Molybdenum and Cobalt Alloys, Analysis of. J. R. Camp and J. W. Marden.... 998
Citric Acid. Tariff Act of 1913. Gov. Pub.... 406
Citrus Seedlings, Response of—in Water Cultures to Salts and Organic Extracts. Breazeale. Gov. Pub.... 308
Clark Standard Cell, Two Common Failures of. McKelvy and Shoemaker. Gov. Pub.... 1139
Clay-Working Industries, Silica Brick and Building Operations in 1918. Middleton. Gov. Pub.... 1033
Clays, American Bond, Properties of—and Use in Graphite Crucibles and Glass Pots. Bleininger. Gov. Pub.... 409
Clays and Shales of Minnesota. Grout. Gov. Pub.... 97
Clays, Stoneware, Properties of. Schurecht. Gov. Pub.... 1033
Coal:
  Original Papers:
    Determination of Sulfur Forms in Coal. A. R. Powell.... 887
    Low Temperature Distillation of Sub-bituminous Coal. H. K. Benson and R. E. Canfield.... 443
    Study of Reactions of Coal Sulfur in Coking Process. A. R. Powell.... 1069
  Government Publications:
    Approved Explosion-Proof Coal Cutting Equipment. Ilsley and Gleim.... 722
    Federal Trade Commission Report.... 96

    House Report.... 511
    In 1917. Part B, Distribution and Consumption, 304; in 1918. Part A, Production. Lesher.... 931
    Prices of—and Coke, 1913–1918. Lesher.... 98
    Safe Storage. Stoek.... 931
Coal Mines:
  Analytical Method for Detecting Blown-Out Shots in. Hutchison and Barab. Gov. Pub.... 99
  Fatalities in U. S., 1919, and Statistics Supplementing Bulletin 115. Fay. Gov. Pub.... 722
  Fatalities in U. S., Monthly Statement of. Adams. Gov. Pub. January 1920, 618; February, 722; March, 823; June, 1139; July. 1221
  Timbering. Virgin. Gov. Pub.... 930
  Ventilation. Virgin. Gov. Pub.... 1032
Coal Tar:
  Chemical Industry. "Nothing to Eat but Food." Editorial.... 314
  Coal-Tar Products. Gov. Pub....96, 617
  Electric Heater for—Naphtha Distillation Test. J. B. Hill and R. B. Chillas.... 280
  Progress of American—Chemical Industry during 1919. G. Jones.... 959
Cobalt. Hess. Gov. Pub., 1917, 1138; 1918.... 823
Cobalt, Molybdenum, and Chromium Alloys, Analysis of. J. R. Camp and J. W. Marden.... 998
Coke, By-Product, Hygroscopicity of. W. A. Selvig and B. B. Kaplan.... 783
Coke, Desulfurizing Action of Hydrogen on. A. R. Powell.... 1077
Coke for Domestic Heating. Kreisinger and Fieldner. Gov. Pub.. 99
Coking of Illinois Coal in Koppers Type Oven. McBride and Selvig. Gov. Pub.... 307
Colloids:
  Ceramic Processes Associated with Colloid Phenomena. A. V. Bleininger.... 436
  Certain Aspects of Chemistry of Cellulose Acetate from Colloidal Viewpoint. G. J. Esselen, Jr.... 801
  Practical Applications of Colloidal Chemistry. J. Alexander.... 434
Combustion Apparatus, New Forms of—for Use in Gas Analysis. E. R. Weaver and P. G. Ledig.... 368
Commerce. Gov. Pub.... 723
COMMERCE REPORTS. October (1919), 100; November, 100; December, 205; January (1920), 409; February, 410; March, 514; April, 619; May, 723; June, 824; July, 931; August, 1034; September, 1139; October.... 1222
Comparator, Improved. L. H. Cooledge.... 499
Concrete Blocks in 1917 and 1918. Loughlin. Gov. Pub.... 512
Concrete Columns, Tests of Eighteen—Reinforced with Cast Iron. Tucker and Bragg. Gov. Pub.... 308
Condensation, Fractional, Purification of Benzoic Acid by. M. Phillips and H. D. Gibbs.... 277
Condenser, New Type of—for Determination of Crude Fiber. C. A. Clemens. (*See* Pickel, 611).... 288
Conductivity Cell, New. F. E. Rice.... 1202
Congressional Committees. Gov. Pub....96, 303, 406, 511, 617, 722, 823, 930
Coniferous Woods, Proximate Analysis of. W. H. Dore.... 476
Cooper Union, Industrial Chemistry at. Note.... 612
Copper-Ammonia-Ammonium Chloride Reagent, Determination of Oxygen by. W. L. Badger.... 161
Copper:
  Alloys with Aluminium and Magnesium. Merica, *et al.* Gov. Pub. 99
  Deposits of Ray and Miami, Arizona. Ransome. Gov. Pub.... 407
  In 1917, 512; in 1918. Butler. Gov. Pub.... 1220
  Peculiar Type of Intercrystalline Brittleness. Rawdon and Langdon. Gov. Pub.... 619
  Production (1917 and 1918). Gov. Pub. Alaska, by Martin; South Dakota, Wyoming, New Mexico and Texas, by Henderson; Central States, by Dunlop and Butler, 97; Eastern States, by Hill; Nevada, by Heikes; Montana, by Gerry; New Mexico and Texas, by Henderson; Arizona, by Heikes; California and Oregon, by Yale; Idaho and Washington, by Gerry; Colorado, by Henderson, 407; Utah, by Heikes, 512; Colorado, by Henderson.... 1138
  Rapid Determination of Small Amounts of—by Iodide Method. H. F. Bradley.... 800
Corn and Corn Meal, Cause of Deterioration and Spoiling of. J. S. McHargue.... 257
Corn, Effect of Mold upon Oil in. F. Rabak.... 46
Corn Oil, Production of—in U. S. Sievers. Gov. Pub.... 1222
Corrosion, Abatement of—in Central Heating Systems. Speller. Gov. Pub.... 99
Corrosion, Cause and Prevention of—on Bores of Firearms. W. J. Huff.... 862
Corrosion of Brass in Dilute Electrolytes. J. H. Reedy and B. Feuer. 541
Corrosive Action. (*See* Chlorine-Treated Water)
Cost Accounting, Value of—in Commercial Laboratories. W. W. Caswell.... 79
Cotton Duck, Waterproofing and Mildewproofing of. Holman, *et al.* Gov. Pub.... 1222
Cottonseed Foots, Heat Balance of Distillation Plant for Recovery of Fatty Acids from. J. Alsberg.... 490
Cottonseed Hulls and Sugar-Cane Fiber, Acid Hydrolysis of. E. C. Sherrard and G. W. Blanco.... 1160
Cottonseed-Oil Products, Kreis Reaction of. W. B. Smith.... 764
Cresol, Purified (Cresylic Acid). H. C. Hamilton.... 50
Cresol Solutions, Saponified. Schaeffer. Gov. Pub.... 723
Cresylic Acid (Purified Cresol). H. C. Hamilton.... 50
Crop and Soil Analysis, Boric Acid Modification of Kjeldahl Method for. F. M. Scales and A. P. Harrison.... 350
Crude Fiber, Determination of—in Prepared Mustard. M. C. Albrech.... 1175
Cryolite and Fluorspar in 1918. Burchard. Gov. Pub.... 307
Crystals, Spherical. Note.... 83
Cupferron, Notes on Preparation of. D. R. Kasanof.... 799
Cupferron, Use of—in Quantitative Analysis. G. E. F. Lundell and H. B. Knowles.... 344
Cuprous Chloride, Convenient Method for Preparation of Hydrochloric Acid Solution of—for Use in Gas Analysis. F. C. Krauskopf and L. H. Purdy.... 158
Cyanamid and Mixed Fertilizers: Rapid, Direct Method for Determination of Dicyanodiamide. R. N. Harger.... 1107
Cyanamid, Changes Taking Place in—When Mixed with Fertilizer Materials. R. N. Harger.... 1111
Cyanide Gas, Adsorption of—by Foodstuffs. Gov. Pub.... 823
Cyanides, Ferrocyanides, and Cyanized Briquets, Production of Ammonia and Formates from. G. W. Heise and H. E. Foote.... 331
Cyanogenesis in Sudan Grass: Modification of Francis-Connell Method of Determining Hydrocyanic Acid. Menaul and Dowell. Gov. Pub.... 409
p-Cymene, Synthesis of Thymol from. M. Phillips and H. D. Gibbs. 733

DARTMOUTH College, New Chemical Laboratory. Editorial Note 1044
Defecation, Recent Advances in. W. D. Horne.... 1179
Department of Agriculture. Gov. Pub....100, 308, 409, 514, 619, 723, 824, 1034, 1139, 1221
Department of Commerce. Gov. Pub.... 723
Department of Interior. Gov. Pub.... 617
Department of Labor. Gov. Pub.... 1220
Department of Navy. Gov. Pub.... 723
Department of State. Gov. Pub.... 823
Department of Treasury. Gov. Pub....723, 823
DeRoode-Perchloric Acid Method for Determining Potash. T. E. Keitt. 276
Desulfurizing Action of Hydrogen on Coke. A. R. Powell.... 1077
Di- and Monoammonium Phosphate, Solubility of. G. H. Buchanan and G. B. Winner.... 448
Diastatic Capacity, Volumetric Method for Determination of. J. T. Flohil.... 677
Diastatic Preparations, New Technical Method for Estimation of Saccharogenic Power of. K. Oshima.... 991
Diazometric Determination of Phenol, and of Certain of Its Homologs. R. M. Chapin.... 568
β,β'-Dichloroethyl Sulfide. (*See* Mustard Gas)
Dicyanodiamide: Rapid, Direct Method for Its Determination in Cyanamid and Mixed Fertilizers. R. N. Harger.... 1107
Diffusing Power of Pigments. W. K. Lewis and F. P. Baker.... 890
Digitalis, Chemistry of. H. C. Hamilton.... 1180
Diphenylamine Test for Nitrates: Some American-Made Chemical Reagents. W. D. Collins.... 801
Disappearance of Dr. Arthur Lachman. Note.... 198
Disinfectants, Hygienic Laboratory Method of Standardizing. Gov. Pub....96, 1033
Distillation Plant, Heat Balance of—for Recovery of Fatty Acids from Cottonseed Foots. J. Alsberg.... 490
Distillation Plants, Tar-Still Operation in Hardwood. L. F. Hawley and H. N. Calderwood, Jr.... 684
Distilling Apparatus, Registration of. Note.... 198
Dourine, Pathology of. Formad. Gov. Pub.... 308
Drawings of Standard Apparatus. W. D. Collins.... 817
Drier, Liquid Paint, Specification for. Gov. Pub.... 1221
Drug Plants under Cultivation. Stockberger. Gov. Pub.... 1222
Drugs. Dumez. Gov. Pub....96, 407
Duralumin, Heat Treatment of. Merica, *et al.* Gov. Pub.... 308
Dust Hazard in Grinding Shops of Ax Factory. Winslow and Greenburg. Gov. Pub.... 1221
Dust Hazard, Protection of Sand Blasters against. Winslow, *et al.* Gov. Pub.... 1221
DYESTUFFS:
  Addresses and Original Papers:
    Detection and Estimation of Yellow AB and Yellow OB in Mixtures. W. E. Mathewson.... 883
    Dye Research. R. E. Rose.... 805
    Hygienic Control of Aniline Dye Industry in Europe. C. Baskerville.... 393
    Progress of American Coal-Tar Chemical Industry during 1919. G. Jones.... 959
  Editorials:
    Chapin Report. (*See* Chapin, 1130).... 1042
    Critical Days.... 107
    Dyes in the Senate.... 210
    Dyestuffs. Note.... 315
    From the Senate Gallery.... 522
    In the Game.... 1147
    Kicking up Dust.... 3
    "Nothing to Eat but Food".... 314
    Reparation Dyes.... 628
    Unfinished Story.... 627
    War Trade Board Licenses. Note.... 1148
  Government Publications:
    Congressional Committee Hearings.... 96
    Dyes and Dyeing....96, 98, 406, 511, 617
    List of References on Dyestuffs. Meyer.... 511
    Prevention of Stream Pollution by Dye and Intermediate Wastes. Casselman....406, 1138
  Notes:
    Dye and Chemical Corporation, Allied.... 1132
    Dye Division, St. Louis Meeting. R. N. Shreve. Announcement, 298; Report.... 609
    Report of E. S. Chapin, Paris Representative of the Textile Alliance, Inc., to the Dye Advisory Committee of the State Department, September 29, 1920. (*See* Editorial, 1042).... 1130

EDITORIALS....2, 107, 210, 314, 522, 626, 730, 834, 1042, 1146
  (*See* HERTY, C. H., in AUTHOR INDEX for Complete List of Titles; Subjects treated are to be found in place in this index)
Education of the Research Chemist. R. E. Rose.... 947
Educational Institutions, Relation of—to Industries. Address, Chicago Meeting, A. C. S. H. P. Talbot.... 943
Educational Institutions, Ten, Thirty-seven Firms, and the Government Service; Study of Economic Status of Chemists in. L. F. Kebler.... 1206
Egg Products, Frozen. Redfield. Gov. Pub.... 824
Eggs, Preservation of—Including Bibliography. H. I. Jones and R. DuBois.... 751
Electric Heater for Coal-Tar Naphtha Distillation Test. J. B. Hill and R. B. Chillas.... 280
Electric Motors, Portable. Note.... 83
Electrolysis of Underground Structures. Shepard. Gov. Pub.... 99
Electrometric Method for Detecting Segregation of Dissolved Impurities in Steel. E. G. Mahin and R. E. Brewer.... 1095
Emulsions, Oil-Field. J. L. Sherrick.... 133
Emulsions, Review of Literature of. A. W. Thomas.... 177
Enameled Cast-Iron Wares, Materials, Methods. Staley. Gov. Pub. 409
Enamels for Sheet Iron and Steel. Shaw. Gov. Pub.... 1221
Engineering and Chemical Laboratories Bibliography. C. J. West.. 295
Engineering Degrees at College of the City of New York. Note.... 613
Engineering Research, Department of—at University of Michigan.... 1214
Engines, Internal Combustion, Comparative Fuel Values of Gasoline and Denatured Alcohol in. Gov. Pub.... 823
Enzymes, Lipolytic, in Olive Oil. T. M. Rector.... 156

Equilibria in Solutions Containing Mixtures of Salts. II—The System Water and Chlorides and Sulfates of Sodium and Magnesium at 25°. W. C. Blasdale.......... 164
Ester Transposition, Influence of—in Determination of Saponification Numbers. A. M. Pardee and E. E. Reid.......... 129
Ether, Note on Catalysis in Manufacture of. H. Schlatter.......... 1101
Ethyl Alcohol and Aniline, Catalysts Which Promote Reaction between. T. B. Johnson, A. J. Hill and J. J. Donleavy.......... 636
Ethylene and Selenium Monochloride, Reaction between. F. H. Heath and W. L. Semon.......... 1100
Exhibition, Great War. Note.......... 389
Explosion, Grain Dust, and Fire Prevention Campaign. Gov. Pub.......... 1139
Explosion of Flashlight Powders. R. H. Kerbs.......... 1026
EXPLOSIVES:
  Development of Liquid Oxygen during War. Gov. Pub.......... 722
  Manufacture of Trinitroxylene for Use as Substitute for TNT in Bursting Charges for High Explosive Shell. J. Marshall.......... 248
  Preparation of Hexanitrodiphenylamine and Use as a Booster for Shell Charges. J. Marshall.......... 336
  Production of—in U. S., 1918. Fay. Gov. Pub.......... 98
  Production of—in U. S., 1919. Adams. Gov. Pub.......... 1221
  Sensitiveness of—to Frictional Impact. Howell. Gov. Pub.......... 99
  Strength and Velocity of Detonation of Various Military Explosives. W. C. Cope.......... 870
  TNT as Blasting Explosive. Munroe and Howell. Gov. Pub.......... 824
EXPOSITION OF CHEMICAL INDUSTRIES, SIXTH NATIONAL:
  New York, September 20 to 25, 1920. Editorial Note, 315; Announcement, 609; Progress Report, 814; General Program, 920; Exhibitors, 921; Report.......... 953
  Opening Address. C. H. Herty.......... 956
  Progress of American Coal-Tar Chemical Industry during 1919. G. Jones.......... 959
  Reorganization of Chemical Warfare Post of American Legion.......... 961
  Abstracts from Meetings.......... 962
Extraction Processes, Numerical Relation between Cells and Treatments in. L. F. Hawley, 493; Correction.......... 613

FABRIC Fastenings. Walen and Fisher. Gov. Pub.......... 96
Fabrics, Airplane, Structure of. Walen. Gov. Pub.......... 303
Fabrics, Balloon, Testing of. Edwards and Moore. Gov. Pub.......... 96
Fabrics, Determination of Water Resistance of. F. P. Veitch and T. D. Jarrell.......... 26
Fabrics: Machinery in Italy. Note.......... 83
Fat and Milk Production, Effect of Drugs. Hays and Thomas. Gov. Pub.......... 824
Fats and Oils, Production and Conservation of—in U. S. Bailey and Reuter. Gov. Pub.......... 100
Fatty Acids, Heat Balance of Distillation Plant for Recovery of—from Cottonseed Foots. J. Alsberg.......... 490
Federal Board for Vocational Education. Gov. Pub..........723, 930, 1032
Federal Trade Commission. Gov. Pub.......... 96
Federated American Engineering Societies. How Best to Serve. Editorial.......... 731
Feldspar in 1918. Beach. Gov. Pub.......... 930
Fellowship at Washington University. Note.......... 298
Fellowships, American Field Service, in French Universities.......... 1214
Fellowships, American, in French Universities. Note.......... 506
Fellowships, Industrial, of Mellon Institute.......... 716
Fermentation, Alcoholic, Quantities of Preservatives Necessary to Inhibit and Prevent—and Growth of Molds. M. C. Perry and G. D. Beal.......... 253
Fermentation Process, Seed-Culture Methods in Production of Acetone and Butyl Alcohol by. H. B. Speakman.......... 581
Fermentation Tube, Smith, Modified Form of. A. V. Fuller.......... 595
Ferrite Crystallization and Inclusions in Steel. II—Solubility of Inclusions. E. G. Mahin and E. H. Hartwig.......... 1090
Ferrocyanides, Cyanides, and Cyanized Briquets, Production of Ammonia and Formates from. G. W. Heise and H. E. Foote.......... 331
Ferrosilicon, Generation of Hydrogen by Reaction between—and Solution of Sodium Hydroxide. E. R. Weaver.......... 232
Ferrosilicon Process for Generation of Hydrogen. Gov. Pub.......... 304
FERTILIZERS:
  Original Papers:
    Changes Taking Place in Cyanamid when Mixed with Fertilizer Materials. R. N. Harger.......... 1111
    Determination of Nitrate Nitrogen in Fertilizers and Nitrates. H. C. Moore.......... 669
    Lindo-Gladding Method, Results of Determination of Potash by. H. C. Moore and R. G. Caldwell.......... 1188
    Rapid, Accurate Method for Determining Nitrogen in Nitrate of Soda by Modified Devarda Method and Use of Davisson Scrubber Bulb. C. A. Butt.......... 352
    Rapid, Direct Method for Determination of Dicyanodiamide in Mixed Fertilizers and Cyanamid. R. N. Harger.......... 1107
    Relative Availability of Nitrate Nitrogen and Commercial Organic Nitrogen. A. W. Blair.......... 262
  Government Publications:
    Atmospheric Nitrogen. Davis.......... 1034
    Crop Injury by Borax. Schreiner, *et al*.......... 619
    Effect of Manure-Sulfur Composts upon Availability of Potassium of Greensand. McCall.......... 824
    Effect of Oxidation of Sulfur in Soils on Solubility of Rock Phosphate and on Nitrification. Shedd. Gov. Pub.......... 308
    Importation, Manufacture, Storage, and Distribution of.......... 308
    Survey of Industry. Goldenweiser.......... 100
Fiber, Crude, New Type of Condenser for Determination of. C. A. Clemens. (*See* Pickel, 611).......... 288
Filter Paper, American-Made. In the Game. Editorial.......... 1147
Filter Paper, Masquerading. Editorial. (*See* Franklin Filter Paper, 955, 1132).......... 1043
Fire Caused by Yellow Phosphorus. H. LeB. Gray, 199; A. Lowy, 507; W. Segerblom.......... 297
Fire Prevention and Grain Dust Explosion Campaign. Gov. Pub.......... 1139
Fire-Proofing Timber. Note.......... 82
Fire-Resistive Construction. Hull. Gov. Pub.......... 205
Firearms, Cause and Prevention of After-Corrosion on Bores of. W. J. Huff.......... 862
Fish, Frozen, Chemical Study of—in Storage. E. D. Clark and L. H. Almy.......... 656
Flame and Bead Tests, Substitutes for Platinum Wire in. C. C. Kiplinger.......... 500
Flashlight Powders, Explosion of. R. H. Kerbs.......... 1026
Flour: Congressional Committee Hearings. Gov. Pub.......... 96
Flour, Hygroscopic Moisture of—Exposed to Atmospheres of Different Relative Humidity. C. H. Bailey.......... 1102
Flour, Microscopical Examination of. Keenan and Lyons. Gov. Pub.......... 514
Flour, Wheat, Heat of Hydration and Specific Heat of. F. Daniels, B. H. Kepner and P. P. Murdick.......... 760
Flour, Wheat, Laboratory Control of—Milling. B. R. Jacobs and O. S. Rask.......... 899
Flue Gas Indicators. Milligan, *et al.* Gov. Pub.......... 931
Fluoride, Ammonium Acid, Titration of. W. S. Chase.......... 567
Fluorspar and Cryolite in 1918. Burchard. Gov. Pub.......... 307
FOODS: (*See* also Cereals, Flour, Fruit, and Sugars)
  Barley, Pearl: Manufacture and Composition. J. A. LeClerc and C. D. Garby.......... 451
  Beverage Samples, Fermentable, Preservatives for. J. S. McCune and A. N. Thurston.......... 689
  Beverages and—, Awards for Theses on. Note.......... 716
  Butter and Allied Products, Volumetric Method for Estimation of Neutralizers in. L. W. Ferris.......... 757
  Corn and Corn Meal, Cause of Deterioration and Spoiling of. J. S. McHargue.......... 257
  Cottonseed-Oil Products, Kreis Reaction of. W. B. Smith.......... 764
  Egg Products, Frozen, Examination of—and Interpretation of Results. Redfield. Gov. Pub.......... 824
  Eggs, Preservation of—Including Bibliography. H. I. Jones and R. DuBois.......... 751
  Fish, Frozen, Chemical Study of—in Storage. E. D. Clark and L. H. Almy.......... 656
  Foodstuffs, Adsorption of Cyanide Gas by. Gov. Pub.......... 823
  Kid, Rabbit, Horse, and Seal Meats, Utilization of—as Food. A. D. Holmes and H. J. Deuel, Jr.......... 975
  Mustard, Prepared, Determination of Crude Fiber in. M. C. Albrech.......... 1175
  Olive Oil, Lipolytic Enzymes in. T. M. Rector.......... 156
  Olives, Botulism from Eating Canned Ripe. Armstrong, *et al.* Gov. Pub..........406, 1032
  Olives, California, Chemical Study of Ripening and Pickling of. Hilts and Hollingshead. Gov. Pub.......... 409
  Orange Beverages, "Fake." Gov. Pub.......... 1138
  Orange Vinegar: Its Manufacture and Composition. H. D. Poore.......... 1176
  Oysters, Pink Yeast Causing Spoilage in. Hunter. Gov. Pub.......... 514
  Shark, Utilization of—for Food and Leather. A. Rogers.......... 293
  Tomato Process of Ripening in—Considered Especially from Commercial Standpoint. Sando. Gov. Pub.......... 1139
  Tomato, Products, Modification of Howard Method for Counting Yeasts, Spores, and Bacteria in. H. M. Miller.......... 766
  Wheat, Effect of Freezing, on Composition of. Blish. Gov. Pub.......... 824
Foreign Exchange Rates. Air-Castles. Editorial.......... 315
FOREIGN INDUSTRIAL NEWS. A. McMillan..........82, 181, 389
Foreign Trade, Our, in Chemicals. O. P. Hopkins.......... 840
Forest Products Laboratory: Decennial Celebration. Note.......... 506
Formaldehyde Method for Determining Ammonium Nitrate. J. T. Grissom.......... 172
Formaldehyde, Solubility of Metals in Acids Containing. R. C. Griffin 1159
Formates and Ammonia, Production of—from Cyanides, Ferrocyanides, and Cyanized Briquets. G. W. Heise and H. E. Foote.......... 331
Formic Acid. Tariff Act of 1913. Gov. Pub.......... 406
France, Sugar Industry of—since the War. T. H. Murphy.......... 1124
French Chemical Industry, Growth of. Note.......... 181
French Gas Warfare. Note.......... 505
Fruit, Chemical Method for Detection in—of Prior Frozen Condition. W. M. Dehn and M. C. Taylor.......... 977
Fruit Juices. Congressional Committee Hearings. Gov. Pub.......... 96
Fruit Juices and Red Wines, Acidimetry of. A. M. Macmillan and A. Tingle.......... 274
Fruit Products: Insoluble Solids in Jams, Preserves, and Marmalades. C. A. Clemens.......... 48
Fuel Briquetting in 1919. Tyron. Gov. Pub.......... 1033
Fuel Deposits in Estland. Note.......... 181
Fuel, New Motor. Note.......... 82
Fuel Oils in Sweden. Note.......... 390
Fuel Value of Volatile Liquid Mixtures. G. Barsky.......... 77
Fuels for Aircraft Engines. Gov. Pub.......... 406
Fuller's Earth in 1918. Middleton. Gov. Pub.......... 204
Fungi, Toxic Action of Gases on. Neifert and Garrison. Gov. Pub.......... 1139
Fungi, Yeast-Like, Action of Ultraviolet Light on. Part I. B. Feuer and F. W. Tanner.......... 740
Furnace, Metal-Melting. Note.......... 389
Furnace, Rosenhain, for Thermal Analysis. Scott and Freeman. Gov. Pub.......... 99
Fusions, Alkali. (*See* Alkali Fusions)

GALLIC, Pyrogallic, and Tannic Acids. Tariff Act of 1913. Gov. Pub.......... 406
GAS:
  Airship and Balloon—Manual. Book 1 and 2. Gov. Pub.......... 1032
  Analysis, Application of Interferometer to. Edwards. Gov. Pub. 99
  Analysis, Automatic Methods of—Depending upon Thermal Conductivity. E. R. Weaver, P. E. Palmer, H. W. Frantz, P. G. Ledig and S. F. Pickering. (*See* Shakespear, 1027).......... 359
  Analysis, Convenient Method for Preparation of Hydrochloric Acid Solution of Cuprous Chloride for Use in. F. C. Krauskopf and L. H. Purdy.......... 158
  Analysis, New Forms of Combustion Apparatus for Use In. E. R. Weaver and P. G. Ledig.......... 368
  French—Warfare. Note.......... 505
  Gas-Mantle, Incandescent, Industry. Gov. Pub.......... 723
  Hydrogen and Inert—, Inflammability of Jets of. P. G. Ledig.......... 1098
  Masks, Procedure for Establishing a List of Permissible. Gov. Pub.......... 722
  Natural, Effect of Gasoline Removal on Heating Value of. Gov. Pub.......... 722
  Natural, Waste and Correct Use of—in the Home. Wyer. Gov. Pub.......... 408
  Oil and—Fires, Extinguishing and Preventing. Bowie. Gov. Pub. 823
  Oil and—in Alamosa Creek Valley, New Mexico. Winchester. Gov. Pub.......... 722
  Oil and—Resources and Structure of Osage Reservation. Goldman. Gov. Pub.......... 931, 1220
  Oil, Water and—, Geochemical Relations of. Sunset-Midway Oil Field, California. Part II. Rogers. Gov. Pub.......... 407
  Tubing, Flexible—, Tests of. McBride and Berry. Gov. Pub.......... 99

GASES:
- Application of Thermal Conductivity Method to Automatic Analysis of Complex Mixtures of. E. R. Weaver and P. E. Palmer... 894
- Compressed, Purification of—in Testing Catalysts for Ammonia Synthesis. R. O. E. Davis.... 289
- Efflux of—through Small Orifices. Buckingham and Edwards. Gov. Pub.... 408
- Permeability of Rubber. Edwards and Pickering. Gov. Pub..... 1139
- Toxic Action of Certain—on Insects, Seeds, and Fungi. Neifert and Garrison. Gov. Pub.... 1139
- Toxic, Use of—for Control of Peach-Tree Borer. Blakeslee. Gov. Pub.... 100

GASOLINE:
- Absorption of—as Applied to Recovery of—in Residual Gas from Compression Plants. Dykema and Neal. Gov. Pub.... 513
- Aviation, Power Characteristics of. Dickinson, *et al.* Gov. Pub... 406
- Denatured Alcohol and—for Internal Combustion Engines. Gov. Pub.... 823
- From Natural Gas:
  - I—Method of Removal. R. P. Anderson.... 547
  - II—Use of Charcoal in Determining the Gasoline Content of Natural Gas. R. P. Anderson and C. E. Hinckley.... 735
  - III—Heating Value, Specific Gravity, and Specific Heat. R. P. Anderson, 852; Correction.... 1028
  - IV—Temperature Correction and Blending Charts. R. P. Anderson, 1011; Correction.... 1214
- Homogeneous and Commercial Aëronautic—, Comparative Test of. Gov. Pub....1032
- Natural Gas—in 1918. Sievers. Gov. Pub.... 1139
- Power Characteristics of Sumatra and Borneo Gasolines. Roberts. Gov. Pub.... 406
- Removal, Effect of—on Heating Value of Natural Gas. Gov. Pub.. 722

Gelatin, Cellulose, and Varnishes, New Turbidimeter for Solutions of. S. E. Sheppard.... 167
Gelatins and Glues, Determination of Jellying Power of—by Polariscope. C. R. Smith.... 878
Gelatins and Glues, Jelly Strength of. S. E. Sheppard, S. S. Sweet and J. W. Scott, Jr., 1007; Correction,.... 1214
General Land Office. Gov. Pub.... 1033
Geochemistry, Data of. Clarke. Gov. Pub.... 512
Geological Survey. Gov. Pub.... 96, 204, 304, 407, 511, 617, 722, 823, 930, 1033, 1139, 1220

GEOLOGY:
- *Government Publications:*
  - Bibliography of North American, 1918. Nickles.... 305
  - General, Shorter Contributions to—, 1918. White.... 98
  - Geothermal Data of U. S. Darton.... 931
  - Gila and San Carlos Valleys, Arizona. Schwennesen.... 304
  - Gradations from Continental to Marine Conditions of Deposition in Central Montana during Eagle and Judith River Epochs. Bowen.... 204
  - San Diego County, Cal. Ellis and Lee.... 204
  - Yellow Pine Cinnabar-Mining District, Idaho. Larsen and Livingston.... 1139

German Books and Periodicals, Purchase of. B. T. Brooks.... 394
Germination of Seeds and Growth of Seedlings. Gov. Pub.... 723

GIBBS MEDAL AWARD:
- Note.... 611
- Presentation Address. W. R. Whitney.... 697
- Address of Acceptance. International Scientific Relations. F. G. Cottrell.... 697

Glass. Gov. Pub....406, 617
Glass, Annealing of. Tool and Valasek. Gov. Pub.... 513
Glass Pots, Use of American Bond Clays in. Bleininger. Gov. Pub. 409

GLUE: (*See* also Casein, Technical)
- Determination of Tensile Strengths of. G. Hopp.... 356
- Influence of Method of Manufacture on Use of Casein in. S. Butterman.... 141
- Manufacture. Note.... 390
- Testing Strength of Jellies. W. H. Low.... 355

GLUES:
- Determination of Jellying Power of—and Gelatins by Polariscope. C. R. Smith.... 878
- Jelly Strength of—and Gelatins. S. E. Sheppard, S. S. Sweet and J. W. Scott, Jr., 1007; Correction.... 1214
- Used in Airplane Parts, with List of References. Allen and Traux. Gov. Pub.... 406

Gold and Silver in 1918. Dunlop. Gov. Pub.... 1033
Gold, Porcupine Placer District, Alaska. Eakin. Gov. Pub.... 407
Gold Production (1917 and 1918). Gov. Pub. Alaska, by Martin; South Dakota, Wyoming, New Mexico and Texas, by Henderson; Kiwalik Koyuk Region, Alaska, by Harrington, 97; Eastern States, by Hill; Nevada, by Heikes; Montana, by Gerry; New Mexico and Texas, by Henderson; Arizona, by Heikes; California and Oregon, by Yale; Idaho and Washington, by Gerry; Colorado, by Henderson, 407; Utah, by Heikes, 512; Colorado, by Henderson.... 1138
Government Chemical Work, Proposed New Departures in.... 1126

GOVERNMENT PUBLICATIONS:
- R. S. McBride....96, 204, 303
- N. A. Parkinson....406, 511, 617, 722, 823, 930, 1032, 1138, 1220

Government Service, Examination of College Trained Chemist for. M. L. Hamlin. (*See* Cotton, THIS JOURNAL, **11** (1919), 1142). 89
Grain-Curd Casein. Studies on Technical Casein—II. W. M. Clark, H. F. Zoller, A. O. Dahlberg and A. C. Weimar.... 1163
Grain-Dust Explosion and Fire Prevention Campaign. Gov. Pub.... 1139
Graphite. Gov. Pub.... 930
Graphite Crucibles, Use of American Bond Clays in. Bleininger. Gov. Pub.... 409
Graphite, Domestic, for Crucibles. Dub and Moses. Gov. Pub.... 823
Graphite in 1918. Ferguson. Gov. Pub.... 306
Graphite Mining in Seward Peninsula, Alaska. Harrington. Gov. Pub.... 97

GRASSELLI MEDAL AWARD:
- Introductory Note, 1127; Abstract from Speech of Acceptance. A. Rogers.... 1128

Grinding Shops, Dust Hazard in. Winslow and Greenburg. Gov. Pub.... 1221
Ground Water. Gov. Pub. Lanfair Valley, California, by Thompson, 407; Nevada and California, by Waring, 931; San Diego Co., California, by Ellis and Lee.... 204
Gum Chicle and Balata, Question of Identity of. (*See* THIS JOURNAL, **11** (1919), 874) C. A. Browne.... 199
Gypsum Deposits of U .S. Stone, *et al.*.... 1220
Gypsum in 1918. Stone. Gov. Pub.... 307

HARDWOOD Distillation Plants, Tar-Still Operation in. L. F. Hawley and H. N. Calderwood, Jr.... 684
Hardwoods, Proximate Analysis of: Studies on *Quercus Agrifolia*. W. H. Dore.... 984
Health Hazards in Industries, Niagara Falls, N. Y. Holmes. Gov. Pub.... 406
Heat Balance of Distillation Plant for Recovery of Fatty Acids from Cottonseed Foots. J. Alsberg.... 490
Heat Insulating Properties of Materials Used in Fire-Resistive Construction. Hull. Gov. Pub.... 205
Heat Transmission, Effect of Air in Steam on Coefficient of. C. S. Robinson, 644; Correction.... 818
Helium. Editorial Note.... 212
Helium. Gov. Pub.... 930
Hematoxylin, Preparation of. P. A. Houseman and C. K. Swift..... 173
Hemp and Ramie, Korean, Proximate Compositions of. Y. Uyeda.. 573
Hess-Ives Tint-Photometer and Its Use with Raw Sugars. G. P. Meade and J. B. Harris.... 686
Hexabromide Method, New, for Linseed Oil. L. L. Steele and F. M. Washburn.... 52
Hexabromide Number, Detection of Oils other than Linseed in Paints by Means of—of Fatty Acids. H. S. Bailey and W. D. Baldsiefen.. 1189
Hexanitrodiphenylamine, Preparation of—and Its Use as Booster for Shell Charges. J. Marshall.... 336
Hide-Tannin Compound, Nature of—and Its Bearing upon Tannin Analysis. J. A. Wilson and E. J. Kern.... 1149
High School Chemistry Teachers, Advanced Work for. W. R. Teeters.... 198
Holmes, Joseph A., Safety Association. Note.... 817
Honey, Artificial. Note.... 389
Hood, Laboratory. J. C. Witt.... 596
Hopkins and Pettit Method, Studies of—for Determining Soil Acidity. Acidity and Acidimetry of Soils—I. H. G. Knight.... 340
Horse Meat, Utilization of—as Food. A. D. Holmes and H. J. Deuel, Jr.... 975
Howard Method, Modification of—for Counting Yeasts, Spores, and Bacteria in Tomato Products. H. M. Miller.... 766
Hydrochloric Acid and Neutral Chlorides, Determination of—in Leather. A. W. Thomas and A. Frieden.... 1186
Hydrochloric Acid, Production of—from Chlorine and Water. H. D. Gibbs.... 538
Hydrocyanic Acid, Modification of Francis-Connell Method of Determining. Menaul and Dowell. Gov. Pub.... 409
Hydrogen and Inert Gas, Inflammability of Jets of. P. G. Ledig.... 1098
Hydrogen and Nitrogen Mixture, Preparation of—by Decomposition of Ammonia. R. O. E. Davis and L. B. Olmstead.... 316
Hydrogen, Desulfurizing Action of—on Coke. A. R. Powell.... 1077
Hydrogen, Ferrosilicon Process for Generation of. Gov. Pub.... 304
Hydrogen, Generation of—by Reaction between Ferrosilicon and Solution of Sodium Hydroxide. E. R. Weaver.... 232
Hydrogen-Ion Concentration, Relationship of—of Natural Waters to Carbon Dioxide Content. R. E. Greenfield and G. C. Baker, 989; Correction.... 1214
Hydrogenated Oils, Use of—in Manufacture of Tin Plate. W. D. Collins and W. F. Clarke.... 149
Hydrometer, Baumé, Notes on. G. H. Taber.... 593
Hygienic Control of Aniline Dye Industry in Europe. C. Baskerville.... 393
Hygienic Laboratory. Gov. Pub....96, 407
Hygienic Laboratory Method of Standardizing Disinfectants. Gov. Pub.... 96
Hygroscopicity of By-Product Coke. W. A. Selvig and B. B. Kaplan 783

ILLUMINATOR, New, for Microscopes. III. A. Silverman...... 1200
Indexing References. A. Tingle.... 909
Indicators and Their Industrial Application. H. A. Lubs.... 273
Indicators Used for Determining Free Acid in Pickling Solutions. C. L. Boyle.... 571
Industrial Alcohol. (*See* Alcohols)
Industrial Chemistry at Cooper Union. Note.... 612
Industrial Coöperation and Research, Division of—of Massachusetts Institute of Technology. W. H. Walker.... 394
INDUSTRIAL NOTES....91, 201, 300, 404, 508, 614, 719, 821, 929, 1030, 1134, 1217
Industrial Survey in U. S., 1919. Willett. Gov. Pub.... 1220
Industrial Wastes, Treatment and Disposal of. Phelps. Gov. Pub... 406
Industries, Relation of Educational Institutions to. Address, Chicago Meeting, A. C. S. H. P. Talbot.... 943
Industries, Value of Technical Training in Reconstruction of. Address, Chicago Meeting, A. C. S. T. E. Wilson.... 941
Inflammability of Jets of Hydrogen and Inert Gas. P. G. Ledig..... 1098
Influenza and Chlorine. C. Baskerville.... 293
Influenza, Chlorine as Preventive of. H. Hale.... 806
Ink Manufacturers. Editorial Note.... 524
Inks: Composition, Manufacture, and Testing of. Gov. Pub.... 931
Insect Powder. McDonnell, *et al.* Gov. Pub.... 723
Insects, Toxic Action of Gases on. Neifert and Garrison. Gov. Pub.... 1139
Instruments and Apparatus, Scientific. Gov. Pub.... 96
Instruments, Scientific, Duty-Free. Playing Their Game. Editorial 1146
Insulating Material, New. Note.... 83
Insulating Material, Varnish for. Note.... 83
Insulating Materials, Thermal Expansion of. Souder and Hidnert. Gov. Pub.... 408
Interferometer, Application of—to Gas Analysis. Edwards. Gov. Pub.... 99
Intermittent Testing Apparatus. Vinal and Ritchie. Gov. Pub.... 1139
INTERNATIONAL CHEMICAL CONFERENCE. C. Lormand.... 925
Invertase Activity of Mold Spores. Kopeloff and Byall. Gov. Pub.. 409
Iodide and Bromide, Determination of—in Mineral Waters and Brines. W. F. Baughman and W. W. Skinner.... 358
Iridium: 1748–1917. Bibliography of Platinum Group Metals. Howe and Holtz. Gov. Pub.... 407
Iron and Steel, Rustproofing of. Gov. Pub.... 100
Iron-Depositing Bacteria. Harder. Gov. Pub.... 98
Iron-Hydroxide and Iron-Oxide Paints, Specification for. Gov. Pub.. 723
Iron, Lead Coated. C. Baskerville.... 152
Iron: Manufacture of Enameled Cast-Iron Wares. Staley. Gov. Pub.... 409
Iron Ore, Deposits near Stanford, Montana. Westgate. Gov. Pub... 1139
Iron Ore, Pig Iron, and Steel in 1918. Burchard. Gov. Pub.... 618
Iron Ore, Rapid Accurate Method for Analysis of. E. Little and W. L. Hults.... 269
Iron, Sheet and Steel, Enamels for. Shaw. Gov. Pub.... 1221

- Isoprene and Toluene, Thermal Decomposition of Turpentine with Particular Reference to Production of. S. A. Mahood.... 1152
- Isotopes. Note.... 389
- ITALIAN CHEMICAL INDUSTRY, IMPRESSIONS OF. C. L. Parsons.... 907
- ITALY, CHEMICAL INDUSTRY AND TRADE OF. O. P. Hopkins.... 525

- JAPAN, CHEMICAL INDUSTRY AND TRADE OF. O. P. Hopkins.... 110
- Jelly. C. H. Campbell.... 558
- Jelly Strength of Gelatins and Glues. S. E. Sheppard, S. S. Sweet and J. W. Scott, Jr., 1007; Correction.... 1214
- Juices, Cane, Relative Importance of Some Coloring Matters in—and Sirups. F. W. Zerban.... 744

- KELP, Potash from. (*See* THIS JOURNAL, **11** (1919), 864)
  - II—Experimental Distillation of Kelp at Low Temperatures. G. C. Spencer.... 682
  - III—The Preliminary Examination of Kelp Distillates. G. C. Spencer.... 786
- Kid Meat, Utilization of—as Food. A. D. Holmes and H. J. Deuel, Jr.... 975
- Kjeldahl Method, Boric Acid Modification of—for Crop and Soil Analysis. F. M. Scales and A. P. Harrison.... 350
- Kjeldahl Nitrogen Determinations, Influence of Potassium Permanganate on. D. C. Cochrane.... 1195
- Koppers Type Oven, Coking in. McBride and Selvig. Gov. Pub.... 307
- Kreis Test, Method of Preparing Phloroglucinol Reagent for. H. W. Dixon.... 174
- Krypton and Xenon, Spectra of. Merrill. Gov. Pub.... 99

- LABORATORIES, Chemical and Engineering, Bibliography. C. J. West.... 295
- Laboratories, Commercial, Value of Cost Accounting in. W. W. Caswell.... 79
- LABORATORY AND PLANT.... 73, 167, 277, 359, 486, 581, 679, 786, 891, 1000, 1197
- Lachman, Dr. Arthur, Disappearance of. Note.... 198
- Lacquer, Shellac, and Shellac Varnish, Rapid Examination of. T. L. Crossley.... 778
- Lactic Acid. Tariff Act of 1913. Gov. Pub.... 406
- Lamps, Flame Safety, and Approved Electric. Virgin. Gov. Pub.... 930
- LEAD:
  - Basic Carbonate White, Specification for. Gov. Pub.... 513
  - Basic Sulfate White, Specification for. Gov. Pub.... 513
  - Hardening Effects of Various Elements upon Lead. C. O. Thieme 446
  - In 1917. Siebenthal. Gov. Pub.... 722, 1220
  - Intercrystalline Brittleness. Rawdon. Gov. Pub.... 824
  - Lead Coated Iron. C. Baskerville.... 152
  - Leaded Zinc Oxide, Specifications for. Gov. Pub.... 408
  - Poisoning, Precautionary Measures to Prevent. Gov. Pub.... 303
  - "Porcelain" White Lead. E. Euston.... 974
  - Production (1917 and 1918). Gov. Pub. Alaska, by Martin; South Dakota, Wyoming, New Mexico and Texas, by Henderson; Central States, by Dunlop and Butler, 97; Eastern States, by Hill; Nevada, by Heikes; Montana, by Gerry; New Mexico and Texas, by Henderson; Arizona, by Heikes; California and Oregon, by Yale; Idaho and Washington, by Gerry; Colorado, by Henderson, 407; Utah, by Heikes, 512; Colorado, by Henderson.... 1138
  - Red, Specifications for. Gov. Pub.... 619
  - White, Modification of Thompson Method for Determination of Acetic Acid in. L. McMaster and A. E. Goldstein.... 170
- LEATHER:
  - *Addresses and Original Papers:*
    - Determination of Hydrochloric Acid and Neutral Chlorides. A. W. Thomas and A. Frieden.... 1186
    - Mechanism of Bating. J. A. Wilson.... 1087
    - Nature of Hide-Tannin Compound and Its Bearing upon Tannin Analysis. J. A. Wilson and E. J. Kern.... 1149
    - Utilization of the Shark. A. Rogers.... 293
  - *Government Publications:*
    - Apparatus for Measuring Relative Wear of Sole Leathers. Hart and Bowker.... 205
    - Effects of Glucose and Salts on Wearing Quality of Sole Leather.. Wormeley, *et al*.... 99
    - Effects of Oils, Greases, and Degree of Tannage on Physical Properties of Russet Harness Leather. Bowker and Churchill.... 824
    - Federal Trade Commission Report.... 96
    - Shoe and—Industries.... 96
    - Sole Leather, Laboratory Wearing Test of. Hart. Gov. Pub.... 1221
- Ledebur Method for Oxygen in Steel. Cain and Adler. Gov. Pub.... 308
- Ledebur Method, Oxygen Content of Deoxidized Acid Bessemer Steels by. Cain and Pettijohn. Gov. Pub.... 308
- Library of Congress. Gov. Pub.... 511
- Liddle, Leonard Merritt. Obituary.... 400
- Life Sciences, Chemistry's Contribution to. Address, Chicago Meeting, A. C. S. A. S. Loevenbart.... 1122
- Lime. Gov. Pub.... 96
  - Effect of—upon Sodium Chloride Tolerance of Wheat Seedlings. LeClerc and Breazeale. Gov. Pub.... 409
  - Effect of Varying Quantities of—upon Yield of Chloropicrin. Control Experiments in Chloropicrin Manufacture—I. H. L. Trumbull, G. T. Sohl, W. I. Burt and S. G. Seaton.... 1068
  - In 1918. Loughlin and Insley. Gov. Pub.... 931
  - Properties and Uses. Gov. Pub.... 1033
  - Quicklime and Hydrated—, Specifications for, for Use in Cooking Rags for Manufacture of Paper. Gov. Pub.... 823
- Lindo-Gladding Method, Results of Determination of Potash by. H. C. Moore and R. G. Caldwell.... 1188
- Linseed Oil, New Hexabromide Method for. L. L. Steele and F. M. Washburn.... 52
- Linseed Oil Substitute. Note.... 82
- Lithium Minerals in 1919. Insley. Gov. Pub.... 1033
- Lithopone, and Barium Chemical Industries. Gov. Pub.... 1138
- LONDON LETTER:
  - S. Miall. (*See* Editorial Notes, 628, 1044).... 819, 928, 1216
- Longworth Bill. From the Senate Gallery. Editorial.... 522
- Lormand, C. Editorial Note.... 732
- Luminous, Self-, Material. Dorsey. Gov. Pub.... 96

- MACMICHAEL Torsional Viscosimeter. W. H. Herschel. (*See* MacMichael, 817).... 282
- Magnesite. Gov. Pub.... 96, 406, 617
- Magnesite in 1918. Yale and Stone. Gov. Pub.... 97
- Magnesium: Alloys of—and Aluminium with Copper, Nickel, and Manganese. Merica, *et al*. Gov. Pub.... 99
- Magnesium and Calcium Carbonates. Conner and Noyes. Gov. Pub.... 308
- Magnesium and Zinc, Reflective Properties of Alloys of—with Aluminium. Waltenberg and Coblentz. Gov. Pub.... 408
- Magnesium: Equilibria in Solutions Containing Mixtures of Salts. II. W. C. Blasdale.... 164
- Magnesium in 1919. Stone. Gov. Pub.... 1033
- Magnetic Analysis, Location of Flaws in Rifle-Barrel Steel by. Sanford and Kouwenhoven. Gov. Pub.... 205
- MANGANESE:
  - *Government Publications:*
    - Alloys with Aluminium and Magnesium. Merica, *et al*.... 99
    - Bronze, Wrought—, Exposed to Corrosion. Merica and Woodward 99
    - Ore: Arizona, by Jones and Ransome, 511; California, by Jones, 511; Colorado, by Jones, 1139; Costa Rica and Panama, 407; Nevada, by Pardee and Jones, 512; New Mexico, by Jones, 205; Wyoming, by Jones, 1139; in 1917, by Hewett, 304; in 1918, by Hewett,.... 618
    - Uses and Production of Ferro-alloys. Weld, *et al*.... 823, 931
  - *Notes:*
    - Manganese in Brazil.... 389
    - Manganese-Zinc Alloy.... 389
- Manihot Seed and Oil. Note.... 182
- Manning, Dr. Van H., Retires. Editorial.... 524
- Manufactures, 1919, Census of. Hartley. Gov. Pub.... 407
- Manufacturing Chemists' Association: Annual Meeting. Note, 712; Note.... 814
- Manure-Sulfur Composts, Effect of—upon Availability of Potassium of Greensand. McCall. Gov. Pub.... 824
- MARKET REPORT. 104, 207, 311, 415, 519, 623, 727, 831, 935, 1039, 1143, 1228
- Market Reports. Editorial Note.... 109
- Massachusetts Institute of Technology. Editorial Note.... 212
- Massachusetts Institute of Technology. Editorial Note. (*See* Walker, 394).... 315
- Massachusetts Institute of Technology, Division of Industrial Cooperation and Research of. W. H. Walker.... 394
- Massachusetts Institute of Technology. The Joy and the Sorrow of M. I. T. Editorial.... 108
- McCrudden Gravimetric Calcium Method Modified. J. O. Halverson and J. A. Schulz.... 77
- MEDALS:
  - Perkin Award. Announcement, 86.... 183
  - Nichols Award. Announcement, 87.... 385
  - Chandler Award.... 599
  - Willard Gibbs Award. Announcement, 611.... 697
  - Remington Honor Medal in Pharmacy. Editorial Note.... 524
  - Grasselli Award.... 1127
- Mellon Institute, Industrial Fellowships of.... 716
- Melting Points, Apparatus for Determination of. L. M. Dennis.... 366
- Melting Points of Chemical Elements. Gov. Pub.... 513
- Menthol and Peppermint Market in Japan. Note.... 182
- Mercury, Determination of. Bouton and Duschak. Gov. Pub.... 722
- Metabolism, Nitrogen, of Steers. Bull and Grindley. Gov. Pub.... 308
- Metal-Mine Accounting. Holmes. Gov. Pub.... 513
- Metallic Impurities, Freeing Fats and Oils from. Note.... 182
- Metallography: Deep Etching of Steel. Rawdon and Epstein. Gov. Pub.... 513
- Metallo-Organic Compounds, Research on—at Northwestern University.... 200
- Metallurgical Materials, Comparison of Accuracy in Analysis of—during Past Twenty-Five Years. E. D. Campbell and G. F. Smith 1020
- METALS:
  - Metals and Nonmetals. Ransome and Burchard. Gov. Pub.... 512
  - Secondary—in 1918. Dunlop. Gov. Pub.... 618
  - Solubility of—in Acids Containing Formaldehyde. R. C. Griffin.. 1159
  - Standard Samples Issued or in Preparation. Gov. Pub.... 513, 1221
  - Tests of—for Industrial Purposes. Gov. Pub.... 96
- Meteorological Tables, Smithsonian. Gov. Pub.... 98
- Methanol: Wood Alcohol No Longer: Hereafter Methanol. C. Baskerville.... 910
- Methyl Orange: Some American-Made Chemical Reagents. W. D. Collins.... 800
- Mica in 1918. Schaller. Gov. Pub.... 931
- Michigan, University of—Department of Engineering Research at.... 1214
- Microscopes, New Illuminator for. III. A. Silverman.... 1200
- Microscopy of Pulverized Ores. Coghill and Bonardi. Gov. Pub.... 99
- Mildew Resistance, Testing—of Textiles. B. S. Levine and F. P. Veitch.... 139
- Milk Production, Effect of Drugs on. Hays and Thomas. Gov. Pub. 824
- Mill, Wire Rod. Note.... 82
- Mine Dust Sampling Apparatus. McElroy. Gov. Pub.... 96
- Mineral Production of U. S., 1917. McCaskey and Clark. Gov. Pub. 931
- Mineral Resources of Alaska. Martin, *et al*. Gov. Pub., 1917, 407; 1918.... 1220
- Mineral Resources of Seward Peninsula, Alaska. Gov. Pub.... 97
- Mineral Resources of U. S. Gov. Pub. 1916, Part I, 304; 1917, Part II, by Loughlin, 722; 1918, Preliminary Report, by Bastin and Clark, 97; 1919, Preliminary Summary, by Loughlin and Clark.... 1138
- Mineral Resources, Work on—Done by U. S. Geological Survey. Bastin and McCaskey. Gov. Pub.... 617
- Mineral Spirits, Volatile, Specifications for—for Thinning Paints. Gov. Pub.... 1139
- Mineral Supplies, Our. Gov. Pub. Bibliography by Wood, 304; McCaskey and Burchard.... 407
- Mineral Waters and Brines, Determination of Iodide and Bromide in. W. F. Baughman and W. W. Skinner.... 358
- Mineral Waters in 1918. Ellis. Gov. Pub.... 512
- Mines, Accident Prevention in—of Butte, Montana. Harrington. Gov. Pub.... 931
- Mines and Quarries, 1919, Census of. Hartley. Gov. Pub.... 407
- Mining and Mineral Industry, Glossary of. Fay. Gov. Pub.... 513
- Mining, General. Callen. Gov. Pub.... 930
- Moisture Content of Cereals. O. A. Nelson and C. A. Hulett.... 40
- Moisture Content, Variation in—of Soils. Martin and Christie. Gov. Pub.... 308
- Moisture, Determination of—in Beet-Sugar Factory Products. V. L. Aikin.... 979
- Moisture, Hygroscopic, of Flour Exposed to Atmospheres of Different Relative Humidity. C. H. Bailey.... 1102
- Molasses, Pycnometer for Density of. Newkirk. Gov. Pub.... 824
- Mold, Effect of—upon Oil in Corn. F. Rabak.... 46
- Mold Spores Contain Enzymes? Coerper. Gov. Pub.... 308

Mold Spores, Effect of Concentration on Deteriorative Activity of—in Sugar. N. Kopeloff, S. Byall and L. Kopeloff........ 256
Mold Spores, Invertase Activity of. Kopeloff and Byall. Gov. Pub. 409
Molds, Quantities of Preservatives Necessary to Inhibit and Prevent Alcoholic Fermentation and Growth of. M. C. Perry and G. D. Beal........ 253
Molybdenum. Hess. Gov. Pub. 1918, 823; 1917........ 1138
Molybdenum, Application of Rotating Zinc Reductor in Determination of. W. Scott........ 578
Molybdenum, Cobalt, and Chromium Alloys, Analysis of. J. R. Camp and J. W. Marden........ 998
Molybdenum, Determination of. Bonardi and Barrett. Gov. Pub.. 1033
Mono- and Diammonium Phosphate, Solubility of. G. H. Buchanan and G. B. Winner........ 448
Monographs, Technologic, American Chemical Society's Series of. (*See* Editorial Note, 1044)........ 195
Montana State College, New Chemistry Building at........ 384
Mortars and Plasters, Measurement of Plasticity of. Emley. Gov. Pub........ 1033
Motor Exhaust Gas, Determination of Carbon Monoxide in Air Contaminated with. M. C. Teague........ 964
Motors, Portable Electric. Note........ 83
Munitions Intoxications in France. Perkins. Gov. Pub........ 96
Mussel Industries of U. S. Coker. Gov. Pub........ 98
MUSTARD GAS:
  Decomposition and Pressure Developed by—in Steel Shell. W. A. Felsing, H. Odeen and C. B. Peterson........ 1063
  Method for Determining Sulfur Monochloride Content of—S_2Cl_2 Mixtures. W. A. Felsing, S. B. Arenson and F. J. Kopp........ 1054
  Precipitation of Sulfur from Crude—by Means of Ammonia. W. A. Felsing and S. B. Arenson........ 1065
  Pressures Produced by Action of Sulfur Monochloride upon β,β'-Dichloroethyl Sulfide. T. G. Thompson and F. J. Kopp........ 1056
  Solubility of β,β'-Dichloroethyl Sulfide in Petroleum Hydrocarbons and Its Purification by Extraction with These Solvents. T. G. Thompson and H. Odeen........ 1057
Mustard, Prepared, Determination of Crude Fiber in. M. C. Albrech........ 1175

NAPHTHA, Coal-Tar, Electric Heater for. Distillation Test. J B. Hill and R. B. Chillas........ 280
Naphthalene Sulfonic Acids:
  I—Some Difficultly Soluble Salts of Certain Naphthalene Sulfonic Acids. J. A. Ambler........ 1081
  II—Method for Qualitative Detection of Some Naphthalene Sulfonic Acids. J. A. Ambler and E. T. Wherry........ 1085
  III—Alternative Method for Qualitative Detection of Naphthalene-2,7- and 1,6-Disulfonic Acids. J. A. Ambler........ 1194
National Academy of Sciences. Gov. Pub........ 1032
National Advisory Committee for Aëronautics. Gov. Pub. 96, 303, 406, 930
NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES (*See* Exposition)
National Foreign Trade Council Report. Note........ 298
NATIONAL RESEARCH COUNCIL:
  Division of Chemistry and Chemical Technology. Meeting, 711; Report of Chairman. W. D. Bancroft, 911; Editorial........ 835
  Editorial Note........ 212
  Fourth Annual Report. Gov. Pub........ 1032
  News Items........ 1213
Natural Gas and Petroleum, 1919, Census. Hartley. Gov. Pub... 407
Natural Gas, Gasoline from. (*See* Gasoline)
Natural-Gas Gasoline in 1918. Sievers. Gov. Pub........ 1139
Naval Stores. Congressional Committee Hearings. Gov. Pub........ 96
Neoarsphenamine, Effect of Shaking—in Air. Roth. Gov. Pub.... 1138
Neutralizers, Volumetric Method for Estimation of—in Butter and Allied Products. L. W. Ferris........ 757
NEW JOURNALS. C. M. Guppy........103, 518, 1227
NEW PUBLICATIONS. C. M. Guppy........103, 206, 310, 414, 518, 622, 726, 830, 934, 1038, 1142, 1227
NICHOLS MEDAL AWARD:
  Announcement, 87; Note........ 385
  Presentation Address. W. H. Nichols........ 385
  Address of Acceptance. I. Langmuir........ 386
Nickel. Hess. Gov. Pub. 1917, 1138; 1918........ 823
Nickel: Alloys with Aluminium and Magnesium. Merica, *et al.* Gov. Pub........ 99
Nickel Deposits in Alaska. Overbeck. Gov. Pub........ 304
Nickel Spark-Plug Electrodes, Deterioration of. Rawdon and Krynitzky. Gov. Pub........ 409
Nitrate, Ammonium, Formaldehyde Method for Determining. J. T. Grissom........ 172
Nitrate Content of Certain Waters Considered Bacteriologically Safe. M. S. Nichols........ 987
Nitrate Industry, Chilean, Potassium Nitrate from. P. F. Holstein. 290
Nitrate Nitrogen and Commercial Organic Nitrogen, Relative Availability of. A. W. Blair........ 262
Nitrate of Soda, Rapid and Accurate Method for Determining Nitrogen in—by Modified Devarda Method and Use of Davisson Scrubber Bulb. C. A. Butt........ 352
Nitrates:
  Determination of—in Commercial Salts, in Pyrotechnics. H. B. Faber and W. B. Stoddard........ 576
  Determination of—in Soil. A. L. Whiting, T. E. Richmond and W. R. Schoonover........ 982
  Determination of Nitrate Nitrogen in—and Fertilizers. H. C. Moore........ 669
  Effect of Chlorides on Nitrometer Determination of. M. T. Sanders........ 169
  Estimation of—and Nitrites in Battery Acid. Sefton. Gov. Pub. 513
Nitric Acid, Absorption of Oxides of Nitrogen by. E. K. Rideal..... 531
Nitric Acid: Commercial Oxidation of Ammonia. G. A. Perley 5, 119
Nitric and Sulfuric Acids, Freezing Points of Mixtures of. W. C. Holmes........ 781
Nitrification, Effect of Oxidation of Sulfur in Soils on. Shedd. Gov. Pub........ 308
Nitrite, Sodium, Melting Point of. Note........ 613
Nitrites and Nitrates in Battery Acid. Sefton. Gov. Pub........ 513
Nitro Compounds, Analysis of Aromatic—by Means of Titanous Chloride. F. L. English........ 994
Nitrocellulose from Wood Pulp. R. G. Woodbridge, Jr........ 380
Nitrogen. Congressional Committee Hearing. Gov. Pub........ 722
Nitrogen, Absorption of Oxides of—by Nitric Acid. E. K. Rideal... 531
Nitrogen and Hydrogen Mixture, Preparation of—by Decomposition of Ammonia. R. O. E. Davis and L. B. Olmstead........ 316
Nitrogen Fixation. A Significant Combination. Editorial........ 107
Nitrogen Fixation. Direct Synthetic Ammonia Process. R. S. Tour 844
Nitrogen Metabolism of Steers. Bull and Grindley. Gov. Pub..... 308
Nitrogen Products Committee Report, British........ 391
Nitrogen, Rapid and Accurate Method for Determining—in Nitrate of Soda, by Modified Devarda Method and Use of Davisson Scrubber Bulb. C. A. Butt........ 352
Nitrometer Determination of Nitrates, Effect of Chlorides on. M. T. Sanders........ 169
Nolan Bill. An Unfinished Story. Editorial........ 627
Nolan Bill. Editorial Note........ 524
Nolan Bill. Hurry Call. Editorial........ 1146
Nolan Bill, H. R. 11984. Relief for the Patent Office. Editorial... 314
Nomenclature, Better Chemical—in Trade Usage. E. J. Crane...... 1026
Northwestern University, Research on Metallo-Organic Compounds at. 200
NORWAY, CHEMICAL INDUSTRIES AND TRADE OF. O. P. Hopkins..... 632
NOTES AND CORRESPONDENCE........87, 197, 293, 391, 505, 611, 713, 815, 1026, 1130, 1213
Noyes, W. A. Society's President for 1920. J. Stieglitz........ 106

OBITUARIES........399, 718
Ocher, Dry and Paste, Recommended Specifications for. Gov. Pub.. 619
Ohio State University, Semi-Centennial Exercises at........ 1213
Oil:
  Corn, Effect of Mold upon Oil in. F. Rabak........ 46
  Corn, Production and Utilization of—in U. S. Sievers. Gov. Pub. 1222
  Cottonseed, Kreis Reaction of—Products. W. B. Smith........ 764
  Determination of Minute Quantities of—in Sulfur. L. S. Bushnell and H. S. Clark........ 485
  Egg, Occurrence of Squalene in—from Shark. M. Tsujimoto...... 73
  Fields. Gov. Pub. Mule Creek, Wyoming, by Hancock, 1033; Sunset-Midway, California, by Pack, 617; Part II, by Rogers, 407; Upton-Thornton, Wyoming, by Hancock........ 722
  Gas and—Fires, Extinguishing and Preventing Bowie. Gov. Pub........ 823
  Gas and—in Alamosa Creek Valley, New Mexico. Winchester. Gov. Pub........ 722
  Gas and—Resources and Structure of Osage Reservation. Goldman. Gov. Pub........931, 1220
  Light, Constant Temperature Still Head for Fractionation of. F. M. Washburn........ 73
  Light, Constant-Temperature Still Head for Fractionation of. Washburn. Gov. Pub........ 100
  Linseed, New Hexabromide Method for. L. L. Steele and F. M. Washburn........ 52
  Linseed, Substitute. Note........ 82
  Manihot, and Seed. Note........ 182
  Oil-Field Emulsions. J. L. Sherrick........ 133
  Olive, Lipolytic Enzymes in. T. M. Rector........ 156
  Prickly Pear Seed. S. Lomanitz........ 1175
  Shale, Distillation of—in Germany. Note........ 82
  Shark Liver, Highly Unsaturated Hydrocarbon (Squalene) in. M. Tsujimoto, 63; Correction........ 395
  Soy-Bean. W. H. Low........ 572
  Soy-Bean, Direct Identification of. C. A. Newhall........ 1174
  Wells, Casing Troubles and Fishing Methods in. Curtin. Gov. Pub........ 1033
  Wells, Perforated Casing and Screen Pipe in. Wagy. Gov. Pub. 722
Oils:
  Fats and—, Freeing—from Metallic Impurities. Note........ 182
  Fats and—, Production and Conservation of—in U. S. Bailey and Reuter. Gov. Pub........ 100
  Fuel—in Sweden. Note........ 390
  Greases,—, and Degree of Tannage, Effects of—on Physical Properties of Russet Harness Leather. Bowker and Churchill. Gov. Pub........ 824
  Heavy Mineral, Determination of Specific Heat of. H. S. Bailey and C. B. Edwards........ 891
  Hydrogenated, Use of—in Manufacture of Tin Plate. W. D. Collins and W. F. Clarke........ 149
  Lubricating, as Purchased by Bureau of Steam Engineering. Gov. Pub........ 723
  Near Thermopolis, Wyoming. Collier. Gov. Pub........ 512
  New Method for Determination of Sulfur in. (*See* 612) C. E. Waters........ 482
  Other than Linseed, Detection of—in Paints, by Means of Hexabromide Number of Fatty Acids. H. S. Bailey and W. D. Baldsiefen........ 1189
  Petroleum and Shale, Utilization of Asphaltic Base Acid Sludge Obtained in Refining. C. Baskerville........ 30
  Petroleum, Rapid Method for the Determination of Sulfur in. A. W. Christie and C. S. Bisson........ 171
  Sulfonated, Determination of Sulfate in. E. J. Kern........ 785
Olive Oil, Lipolytic Enzymes in. T. M. Rector........ 156
Olives, California, Chemical Study of Ripening and Pickling of. Hilts and Hollingshead. Gov. Pub........ 409
Olives, Canned Ripe, Botulism from Eating. Armstrong, *et al.* Gov. Pub........ 1032
Opium. Gov. Pub........ 407
Orange Beverages, "Fake." Gov. Pub........ 1138
Orange Vinegar: Its Manufacture and Composition. H. D. Poore. 1176
Ore Deposits of Utah. Butler, *et al.* Gov. Pub........ 931
Organic Chemists, Qualifications of. M. L. Crossley........ 951
Organic Emulsions and Petroleum, Convenient Method for Determination of Water in. E. W. Dean and D. D. Stark........ 486
Organic Nitrogen and Nitrate Nitrogen, Relative Availability of Commercial. A. W. Blair........ 262
ORIGINAL PAPERS..5, 119, 228, 316, 443, 531, 636, 733, 844, 964, 1069, 1149
Osmium:
  1748–1917. Bibliography of Platinum Group Metals. Howe and Holtz. Gov. Pub........ 407
Oxalic Acid. Tariff Act of 1913. Gov. Pub........ 406
Oxygen, Determination of—by Copper-Ammonia-Ammonium Chloride Reagent. W. L. Badger........ 161
Oxygen, Excess, Method for Determination of Oxygen Demand of Sewage and Industrial Wastes. Theriault. Gov. Pub........ 723
Oxygen, Indicators for—in Air and Flue Gas. Milligan, *et al.* Gov. Pub........ 931
Oxygen, Liquid, Development of—Explosives during War. Gov. Pub........ 722
Oysters, Pink Yeast Causing Spoilage in. Hunter. Gov. Pub...... 514
Ozone in Ventilation. Gov. Pub........617, 1221

PAINT, Black, Specification for. Gov. Pub........ 723
Paint, Green, Specifications for. Gov. Pub........ 1033

Paint, White and Tinted, Made on a White Base, Specifications for. Gov. Pub. 513
Paints, Detection of Oils other than Linseed in—by Means of Hexabromide Number of Fatty Acids. H. S. Bailey and W. D. Baldsiefen 1189
Paints, Iron-Oxide and Iron-Hydroxide, Specification for. Gov. Pub. 723
Paints: Recommended Specifications for Volatile Mineral Spirits for Thinning Paints. Gov. Pub. 1139
Palladium: 1748–1917. Bibliography of Platinum Group Metals. Howe and Holtz. Gov. Pub. 407
Paper. Gov. Pub. 617, 823
Paper-Making from Bagasse. Note 83
Paper, Specifications for Quicklime and Hydrated Lime for Use in Cooking Rags for Manufacture of. Gov. Pub. 823
Paracoumarone Resin, Use of—in Varnishes. W. W. King, F. W. Bayard and F. H. Rhodes 549
PARIS LETTER. C. Lormand 820, 1029, 1134, 1217
Patent Office. Editorial Note 1044
Patent Office: Hurry Call. Editorial 1146
Patent Office, Relief for. Editorial 314
Patent Service, Inadequate. Editorial 212
Patents. An Unfinished Story. Editorial 627
Patents. Editorial Note 524
Pearl Barley: Manufacture and Composition. J. A. LeClerc and C. D. Garby 451
Peat. Gov. Pub. 1918, by Osbon, 304; 1919, by Cottrell 1220
Peat in Dismal Swamp of Virginia and North Carolina. Osbon. Gov. Pub. 97
Peat Material, Quality and Value of. Dachnowski. Gov. Pub. 409
Pellagra Incidence, Study of Relation of Factors of Sanitary Character to. Goldberger, *et al.* Gov. Pub. 930
Peppermint and Menthol Market in Japan. Note 182
PERKIN MEDAL AWARD:
  Announcement, 86; Note 183
  Personalities. M. C. Whitaker 183
  Presentation Address. M. T. Bogert 184
  Address of Acceptance. C. F. Chandler 189
Permanganate, Potassium, Influence of—on Kjeldahl Nitrogen Determinations. D. C. Cochrane 1195
Permanganate Titrations, Note on Catalysis of. P. H. Segnitz 1196
PERSONAL NOTES 93, 203, 300, 401, 510, 616, 721, 822, 930, 1031, 1136, 1219
Petroleum:
  Convenient Method for Determination of Water in—and Other Organic Emulsions. E. W. Dean and D. D. Stark 486
  Rapid Method for Determination of Sulfur in—Oils. A. W. Christie and C. S. Bisson 171
  Specific Heat of—at Different Temperatures. F. W. Bushong and L. L. Knight 1197
  Utilization of Asphaltic Base Acid Sludge Obtained in—Refining and Shale Oils. C. Baskerville 30
  Government Publications:
    Bibliography of—and Allied Substances, 1917. Burroughs 1221
    Census of—and Natural Gas, 1919. Hartley 407
    Petroleum. 617, 823, 930; in 1918, Lloyd 1138
    Removal of Lighter Hydrocarbons from—by Continuous Distillation. Wadsworth 408
    Specifications, Report of Fuel Administration Committee on Standardization of. December 1918, 407; November 1919 407
    World's Production. Gov. Pub. 407
Pharmacopoeia, Relation of Chemist to U. S. C. H. LaWall 696
PHARMACOPOEIAL CONVENTION, U. S.:
  11th Decennial Meeting, Washington, D. C., May 11 to 13, 1920. 712
Pharmacy, Award of Remington Honor Medal in. Editorial Note 524
Phenol, Diazometric Determination of—and Certain of Its Homologs. R. M. Chapin 568
Phenol, Manufacture of—in Continuous High Pressure Autoclave. K. Brown 279
Phenol, New Method for Determination of—in Presence of Certain Other Phenols. R. M. Chapin 771
Phenolphthalein, Behavior of—with Iodine, and Method for Determination of. S. Palkin 766
Phillips, F. C. Editorial Note, 212; Obituary 399
Phloroglucinol Reagent, Method of Preparing—for Kreis Test. H. W. Dixon 174
Phosgene, Preparation of Arsenic Trichloride from—and White Arsenic. L. H. Milligan, W. A. Baude and H. G. Boyd 221
Phosphate Leases and Use of Permits, Regulations concerning. Gov. Pub. 1033
Phosphate, Mono- and Diammonium, Solubility of. G. H. Buchanan and G. B. Winner 448
Phosphate, Rock, Effect of Oxidation of Sulfur in Soils on Solubility of. Shedd. Gov. Pub. 308
Phosphate Rock in 1918. Stone. Gov. Pub. 98
Phosphoric Acid, Production of—by Smelting Phosphate Rock in Fuel-Fed Furnace. W. H. Waggaman and T. B. Turley 646
Phosphorus, Yellow, Fire Caused by. H. LeB. Gray, 199; A. Lowy, 507; W. Segerblom 297
Photobibliographic Research Methods: Compilation of Technical Data with Aid of Photography. A. Worischek 679
Photometer, Tint-, Hess-Ives, and Its Use with Raw Sugars. G. P. Meade and J. B. Harris 686
Phthalate, Cellulose. H. A. Levey 743
Phthalic Anhydride. IV—Vapor Pressure of. K. P. Monroe. (*See* THIS JOURNAL, **11** (1919), 1031, 1116, and 1119) 969
Phthalic Anhydride, Pure, History of Preparation and Properties of. H. D. Gibbs 1017
Phytochemical Research, New Fields of. E. Kremers 1018
Pickering Sprays. Cook. Gov. Pub. 1034
Pickling Solutions, Indicators Used for Determining Free Acid in. C L. Boyle 571
Pigments, Diffusing Power of. W. K. Lewis and F. P. Baker 890
Plant, Relation of Concentration and Reaction of Nutrient Medium to Growth and Absorption of. Hoagland. Gov. Pub. 308
Platinum: 1748–1917. Bibliography of Platinum Group Metals. Howe and Holtz. Gov. Pub. 407
Platinum and Allied Metals. Gov. Pub. Hill. 1918, 305; 1919 1033
Platinum and Gold Placers of Kiwalik-Koyuk Region, Alaska. Harrington. Gov. Pub. 97
Platinum Theft, Uncovering—at Old Hickory Power Plant, Jacksonville, Tennessee 815
Platinum Thefts. Note 90, 199, 613, 1028
Platinum Wire, Substitutes for—in Bead and Flame Tests. C. C. Kiplinger 500
Polarization Method, Double, for Sucrose Estimation and Evaluation of Clerget Divisor. Jackson and Gillis. Gov. Pub. 823
Polarization Methods, Double, Notes on—for Determination of Sucrose, and Suggested New Method. G. Rolfe and L. F. Hoyt 250
Polarizing, Changes in—Constants of Sugars during Refining. A. F. Blake 1104
Pollution of City Water Supply Enjoined. Gov. Pub. 96
Pollution, Prevention of Stream—by Dye and Intermediate Wastes. Casselman. Gov. Pub. 406
Pond, George Gilbert. Obituary. W. H. W. 718
Pope, Sir W. J. Editorial Note 732
Positions for Ex-Service Men 298
Potash:
  Deposits. Gale. Gov. Pub. In Alsace, 931; in Spain 931
  DeRoode-Perchloric Acid Method for Determining Potash. T. E. Keitt 276
  From Kelp. (*See* Kelp)
  From a New Angle. Editorial 834
  In 1918. Hicks. Gov. Pub. 618
  Results of Determination of—by Lindo-Gladding Method. H. C. Moore and R. G. Caldwell 1188
  Soluble, United States' Search for Natural Deposits of. H. D. Ruhm 837
Potassium and Calcium Sulfates, Formation of Double Salts of—at 100° C. E. Anderson and R. J. Nestell 243
Potassium, Effect of Manure-Sulfur Composts upon Availability of—of Greensand. McCall. Gov. Pub. 824
Potassium Ferricyanide: Some American-Made Chemical Reagents. W. D. Collins 800
Potassium Nitrate from Chilean Nitrate Industry. P. F. Holstein 290
Potassium Permanganate, Influence of—on Kjeldahl Nitrogen Determinations. D. C. Cochrane 1195
Potassium Salts. Congressional Committee Hearings. Gov. Pub. 96
Pottery in 1918. Middleton. Gov. Pub. 305
Pratt, David Shepard. Obituary 400
Preservatives for Fermentable Beverage Samples. J. S. McCune and A. N. Thurston 689
Preservatives, Quantities of—Necessary to Inhibit and Prevent Alcoholic Fermentation and Growth of Molds M. C. Perry and G. D. Beal 253
Preserves, Jams, and Marmalades, Insoluble Solids in. C. A. Clemens 48
Prickly Pear Seed, Oil of. S. Lomanitz 1175
Priestley, Dr. Joseph, Bookplate of. C. A. Browne 611
Protein Catabolism and Fatigue. Scott and Hastings. Gov. Pub. 1221
Public Health Service. Gov. Pub. 96, 303, 406, 511, 617, 723, 823, 930, 1032, 1138, 1221
Pycnometer for Density of Molasses. Newkirk. Gov. Pub. 824
Pyrites and Sulfur in 1918. Smith. Gov. Pub. 305
Pyrogallic Acid. Tariff Act of 1913. Gov. Pub. 406
Pyroligneous Acid, Determination of Acetic Acid in. V. E. Grotlisch. 1183
Pyrotechnics, Short Commercial Analytical Methods for Determination of Purity of Important Chemicals Used in. H. B. Faber and W. B. Stoddard 576
Pyroxylin Solutions, Measurement of Viscosity of. E. F. Higgins and E. C. Pitman 587

QUARRY Accidents in U. S., 1918. Fay. Gov. Pub. 722
Quicklime and Hydrated Lime, Specifications for—for Use in Cooking Rags for Manufacture of Paper. Gov. Pub. 823
Quicksilver in 1918. Ransome. Gov. Pub. 306

RABBIT Meat, Utilization of—as Food. A. D. Holmes and H. J Denel, Jr. 975
Radiation, Constants of—of Uniformly Heated Inclosure. Coblentz. Gov. Pub. 408
Radiation, Methods for Computing and Intercomparing—Data. Coblentz. Gov. Pub. 408
Radium. Hess. Gov. Pub. 1917, 1138; 1918 823
Radium, Practical Methods for Determination of. III—Alpha-Ray Method, Gamma-Ray Method, Miscellaneous. S. C. Lind. (*See* THIS JOURNAL, **7** (1915), 406, 1024) 469
Railroad Administration. Lost Ground to Be Recovered. Editorial. 210
Ramie and Hemp, Korean, Proximate Compositions of Y. Uyeda 573
Ramsay Memorial Fund. Note 298
Rare-Earth Minerals, Thorium, and Zirconium, 1919. Schaller. Gov. Pub. 1033
READING COURSES, CHEMICAL. W. A. Hamor, L. C. Newell, A. M. Patterson, and W. Segerblom. (*See* McClelland, 1026) 701, 806
Reagents, Unit Weights for Purchase of. W. D. Collins 1206
RECENT JOURNAL ARTICLES. C. M. Guppy 103, 206, 310, 414, 518, 622, 726, 830, 934, 1038, 1142, 1227
Reconstruction Aspects of Some Chemical Industries in U. S. E. Gudeman 376
Red Lead, Recommended Specifications for. Gov. Pub. 619
Registration of Stills. Note 198
Remington Honor Medal in Pharmacy, Award of. Editorial Note 524
Research Chemist, Education of. R. E. Rose 947
Research, Plan for Incentive to—in Pure and Applied Chemistry. W. J. Hale 690
Resistance, Water, Determination of—of Fabrics. F. P. Veitch and T. D. Jarrell 26
Resorcinol, Fusion of Sodium Benzene *m*-Disulfonate with Sodium Hydroxide for Production of. Alkali Fusions—II. M. Phillips and H. D. Gibbs, 857; Correction 1028
Rhodium: 1748–1917. Bibliography of Platinum Group Metals. Howe and Holtz. Gov. Pub. 407
Rice, Red: Laboratory Experiments on Manufacture of Chinese Ang-Khak in U. S. M. B. Church 45
Rock, Phosphate, 1918. Stone. Gov. Pub. 98
Rope-Making. Editorial, 626; Editorial Note 732
Rubber:
  Action of Certain Organic Accelerators in Vulcanization of G. D. Kratz, A. H. Flower and C. Coolidge 317
  Aging of Certain—Compounds. I. R. Ruby and H. A. Depew 1155
  Determination of Cellulose in—Goods. Epstein and Moore. Gov. Pub. 513
  Determination of True Free Sulfur and True Coefficient of Vulcanization in Vulcanized Rubber. W. J. Kelly 875
  Direct Determination of India—by Nitrosite Method. Tuttle and Yurow. Gov. Pub. 100
  Direct Method for Determination of Rubber Hydrocarbon in Raw and Vulcanized Rubber. W. K. Lewis and W. H. McAdams 673

- Effect of Certain Accelerators upon Properties of Vulcanized Rubber—II. G. D. Kratz and A. H. Flower 971
- Expansion of—Compounds during Vulcanization. C. W. Sanderson 37
- Extraction of—Goods. Epstein and Gonyo. Gov. Pub 824
- Microsections Cut from Vulcanized—Articles. H. A. Depew and I. R. Ruby 1156
- Permeability to Gases. Edwards and Pickering. Gov. Pub 1139
- Reactions of Accelerators during Vulcanization. C. W. Bedford and W. Scott 31
- Volume Increase of Compounded—under Strain. H. F. Schippel. 33

Ruthenium: 1748–1917. Bibliography of Platinum Group, Metals. Howe and Holtz. Gov. Pub 407

SACCHARIMETERS, Testing of—by Means of Telescopic Control Tube. C. A. Browne 792
Saccharine. Editorial Note 109
Saccharogenic Power, New Technical Method for Estimation of—of Diastatic Preparations. K. Oshima 991
Salt, Bromine, and Calcium Chloride in 1918. Stone. Gov. Pub 98
Sampler, Modified Boerner. Boerner. Gov. Pub 1034
Sand and Gravel in 1918. Stone. Gov. Pub 307
Sand Blasters, Protection of—against Dust Hazard. Winslow, *et al.* Gov. Pub 511, 1221
Sanitation, Rural, Increasing Efficiency of. Robinson. Gov. Pub 1138
Saponification Numbers, Butyl Alcohol as Medium for Determination of. A. M. Pardee, R. L. Hasche and E. E. Reid 481
Saponification Numbers, Influence of Ester Transposition in Determination of. A. M. Pardee and E. E. Reid 129
Scales, Railroad Track, Specifications for. Gov. Pub 513
Sciences, Life, Chemistry's Contribution to. Address, Chicago Meeting, A. C. S. A. S. Loevenhart 1122
Scientific Literature, International Catalog of. Gov. Pub 406
SCIENTIFIC SOCIETIES. .84, 195, 395, 500, 608, 705, 812, 911, 1022, 1126
Seal Meat, Utilization of—as Food. A. D. Holmes and H. J. Deuel, Jr 975
Seeds, Toxic Action of Gases on. Neifert and Garrison. Gov. Pub. 1139
Selenium. Hill. Gov. Pub., 304; 1919 1139
Selenium and Tellurium. V. Lenher 597
Selenium Monochloride and Ethylene, Reaction between. F. H. Heath and W. L. Semon 1100
Serum, Antimeningococcic, Determination of Bacteritropic Content of. Evans. Gov. Pub 96
Sewage and Industrial Wastes, Excess Oxygen Method for Determination of Oxygen Demand of. Theriault. Gov. Pub 723
Sewage, Studies of Methods for Treatment and Disposal of. Phelps. Gov. Pub 406
Sewage, Treatment and Disposal of. Hommon, *et al.* Gov. Pub. 406, 1138
Sewage, Treatment of—from Single Houses and Small Communities. Frank and Rhynus. Gov. Pub 406
Shale, Oil, Distillation of—in Germany. Note 82
Shale Oils and Petroleum, Utilization of Asphaltic Base Acid Sludge Obtained in Refining. C. Baskerville 30
Shales and Clays of Minnesota. Grout. Gov. Pub 97
Shark Liver Oil, Highly Unsaturated Hydrocarbon (Squalene) in. M. Tsujimoto, 63; Correction 395
Shark, Occurrence of Squalene in Egg Oil from. M. Tsujimoto 73
Shark, Utilization of—for Food and Leather A. Rogers 293
Shellac, Shellac Varnish, and Lacquer, Rapid Examination of. T. L. Crossley 778
Silage, Experimental, Influence of Fermentation on Starch Content of. Dox and Yoder. Gov. Pub 824
Silage, Sunflower. Neidig and Vance. Gov. Pub 308
Silica Brick, 1918. Middleton. Gov. Pub 1033
Silica in 1918. Katz. Gov. Pub 306
Silicate and Carbonate Rocks, Analysis of. Hillebrand. Gov. Pub 305, 407
Silicate of Soda: Colloidal Method for Increasing Volume of Adhesive Water-Glass 174
Silver and Gold in 1918. Dunlop. Gov. Pub 1033
Silver Production (1917 and 1918). Gov. Pub. Alaska, by Martin; South Dakota, Wyoming, New Mexico and Texas, by Henderson; Central States, by Dunlop and Butler, 97; Eastern States, by Hill; Nevada, by Heikes; Montana, by Geary; New Mexico and Texas, by Henderson; Arizona, by Heikes; California and Oregon, by Yale; Idaho and Washington, by Gerry; Colorado, by Henderson, 407; Utah, by Heikes, 512; Colorado, by Henderson 1138
Sirups, Relative Importance of Some Coloring Matters in—and Cane Juices. F. W. Zerban 744
Slate in 1918. Loughlin and Coons. Gov. Pub 204
Smith, Edgar Fahs. A Life of Service. Editorial 211
Smith Fermentation Tube, Modified Form of. A. V. Fuller 595
Smithsonian Institution. Gov. Pub 98, 406
Soapstone and Talc in 1918. Diller. Gov. Pub 618
Société de Chimie Industrielle. Editorial Note 109
- New York Section Meeting, May 14, 1920 608

SOCIETY OF CHEMICAL INDUSTRY:
- American Section. Perkin Medal, 86, 183; Grasselli Medal, 1127; Joint Meeting, October 15, 1920 1126
- Canadian Hospitality. Editorial 626
- Election of Sir W. J. Pope to President. Editorial Note 732

Society of Cotton Products Analysts:
- 11th Annual Convention, New Orleans, La., May 10 and 11, 1920. Report 610

Soda Lime as Absorbent for Industrial Purposes. R. E. Wilson 1000
Sodium Amalgam, Simple Method for Preparation of—in Flakes. A. D. Hirschfelder and M. C. Hart 499
Sodium and Sodium Compounds in 1918. Wells. Gov. Pub 306
Sodium Benzene *m*-Disulfonate, Fusion of—with Sodium Hydroxide for Production of Resorcinol. Alkali Fusions—II. M. Phillips and H. D. Gibbs, 857; Correction 1028
Sodium Chloride, Effect of Lime upon—Tolerance of Wheat Seedlings. LeClerc and Breazeale. Gov. Pub 409
Sodium *p*-Cymene Sulfonate, Fusion of—with Sodium Hydroxide for Production of Carvacrol. Alkali Fusions—I. H. D. Gibbs and M. Phillips. (*See* Hixson and McKee, 296) 145
Sodium, Determination of—in Pyrotechnics in Presence of Potassium. H. B. Faber and W. B. Stoddard 576
Sodium: Equilibria in Solutions Containing Mixtures of Salts—II. W. C. Blasdale 164
Sodium Mining Leases and Prospecting Permits, Regulations concerning. Gov. Pub 1033
Sodium Nitrite, Melting Point of. Note 613
Soil and Crop Analysis, Boric Acid Modification of Kjeldahl Method for. F. M. Scales and A. P. Harrison 350
Soil Constituents at Successive Stages of Plant Growth, Rate of Absorption of. Burd. Gov. Pub 308
Soil Extracts, Solid Phases Obtained by Evaporation of Certain. M. S. Anderson and W. H. Fry 663

SOILS:
- Acidity and Acidimetry of:
  - I—Studies of Hopkins and Pettit Method for Determining Soil Acidity. H. G. Knight 340
  - II—Investigation of Acid Soils by Means of the Hydrogen Electrode. H. G. Knight 457
  - III—Comparison of Methods for Determining Lime Requirements of Soils with Hydrogen Electrode. IV—Proposed Method for Determination of Lime Requirements of Soils. H. G. Knight 559
- Carbonates of Calcium and Magnesium in Relation to Chemical Composition, Bacterial Contents, and Crop-Producing Power of Very Acid Soils. Conner and Noyes. Gov. Pub 308
- Determination of Nitrates. A. L. Whiting, T. E. Richmond and W. R. Schoonover 982
- Effect of Calcium Sulfate on Solubility. McCool and Millar. Gov. Pub 723
- Effect of Variation in Moisture Content on Water-Extractable Matter. Martin and Christie. Gov. Pub 308
- Magnesium and Calcium Carbonates in Relation to Acid Soils. Conner and Noyes. Gov. Pub 308

Solder, Tin-, Substitutes. Note 390
Solderers, Acid Burns on Hands of. Keatley. Gov. Pub 1138
Solvay, M. Ernest, Presentation of Honorary Membership Certificate to. Note 712
Sorghum, Plant Composition of. Willaman, *et al.* Gov. Pub 308
Soy-Bean Leaves, Chemical Study of Ether Extracts of. E. M. Nelson 49
Soy-Bean Oil. W. H. Low 572
Soy-Bean Oil, Direct Identification of. C. A. Newhall 1174
SPAIN. CHEMICAL INDUSTRY AND TRADE OF. O. P. Hopkins 223, 298
Spark Plugs, Ceramic Insulators for. Gov. Pub 304
Spark Plugs Having Steel and Brass Shells, Temperatures in. Gov. Pub 304
Sparking Voltage, Effect of Temperature and Pressure on. Loeb and Silsbee. Gov. Pub 304
Specific Heat, Determination of—of Heavy Mineral Oils. H. S. Bailey and C. B. Edwards 891
Spectrophotometry, Photoelectric, Null Method of. Gibson. Gov. Pub. 99
Spectrum of Acetylene Flame, Distribution of Energy in. Coblentz. Gov. Pub 408
Spherical Crystals. Note 83
Spruce Struts, Compressive Strength of—and Derivation of Formulas for Airplane Design. Boyd. Gov. Pub 619
Squalene: Highly Unsaturated Hydrocarbon in Shark Liver Oil. M. Tsujimoto, 63; Correction 395
Squalene, Occurrence of—in Egg Oil from Shark. M. Tsujimoto 73
Steam, Effect of Air in—on Coefficient of Heat Transmission. C. S. Robinson, 644; Correction 818
"Stearic" Acids, Commercial, Uniform Composition of—and Its Explanation. B. H. Nicolet 677

Steel:
- Determination of Zirconium in Steel. G. E. F. Lundell and H. B. Knowles 562
- Effects of—on Equilibrium: $Cl_2 + H_2O \rightleftharpoons HCl + HClO$, and of Products of Equilibrium on Steel. Studies on Corrosive Action of Chlorine-Treated Water—I. G. L. Clark and R. B. Iseley 1116
- Electrometric Method for Detecting Segregation of Dissolved Impurities in Steel. E. G. Mahin and R. E. Brewer 1095
- Inclusions and Ferrite Crystallization in Steel. II—Solubility of Inclusions. E. G. Mahin and E. H. Hartwig 1090
- *Government Publications:*
  - Electrolytic Resistance Method for Determining Carbon in Steel. Cain and Maxwell 308
  - Enamels for—and Sheet Iron. Shaw 1221
  - Iron Ore—and Pig Iron in 1918. Burchard 618
  - Location of Flaws in Rifle-Barrel—by Magnetic Analysis. Sanford and Kouwenhoven 205
  - Metallographic Features Revealed by Deep Etching. Rawdon and Epstein 513
  - Oxygen Content by Ledebur Method of Deoxidized Acid Bessemer Steels. Cain and Pettijohn 308
  - Rustproofing of—and Iron 100

Stenches as Warning in Mines. Katz, *et al.* Gov. Pub 931
Still Head, Constant Temperature—for Light Oil Fractionation. F. M. Washburn, 73; Gov. Pub 100
Stone in 1918. Loughlin and Coons. Gov. Pub 1220
Stream Pollution, Prevention of—by Dye and Intermediate Wastes. Casselman. Gov. Pub 1138
Strontium in 1918. Stose. Gov. Pub 618

SUGAR:
- *Addresses and Original Papers:*
  - Acid Hydrolysis of Sugar-Cane Fiber and Cottonseed Hulls. E. C. Sherrard and G. W. Blanco 1160
  - American Progress in Bacteriological Sugars. E. H. Eitel 1202
  - Beet-Sugar Industry, Chemical Control in. S. J. Osborn 803
  - Bone-Black and Decolorizing Carbons. W. D. Horne 1015
  - Cane Juices and Sirups, Relative Importance of Some Coloring Matters in. F. W. Zerban 744
  - Changes in Polarizing Constant of—during Refining. A. F. Blake 1104
  - Deterioration of Cuban Raw—in Storage N. Kopeloff and H. Z. E. Perkins 555
  - Determination of Moisture in Beet—Factory Products. V. L. Aikin 979
  - Effect of Concentration on Deteriorative Activity of Mold Spores. N. Kopeloff, S. Byall and L. Kopeloff 256
  - Effect of Varying Amount of Inoculum and Concentration on Deterioration of—by Molds. N. Kopeloff 455
  - Hess-Ives Tint-Photometer and Its Use with Raw Sugars. G. P. Meade and J. B. Harris 686
  - Industry of France since War. T. H. Murphy 1124
  - Notes on Double Polarization Methods for Determination of Sucrose, and a Suggested New Method. G. W. Rolfe and L. F. Hoyt 250
  - Preservation of Bagasse in Sugar-Cane Mill Control. G. L. Spencer 1197
  - Prevention of—Deterioration by Use of Superheated Steam in Centrifugals. N. Kopeloff, 860; Correction 1028
  - Recent Advances in Defecation. W. D. Horne 1179

  Sirup from Home-Grown Sugar Beets. J. M. Ort and J. R. Withrow.......... 154
Government Publications:
  Beet-Top Silage and Other By-Products of the—Beet. Jones. 409
  Cane Juice Clarification for Sirup Manufacture. Dale and Hudson.......... 1222
  Double Polarization Method for Estimation of Sucrose and Evaluation of Clerget Divisor. Jackson and Gillis.......... 823
  Molasses, New Pycnometer for Determining Density of. Newkirk.......... 824
  Mosaic Disease of Sugar Cane and Other Grasses. Brandes.... 100
  Sorghum, Plant Composition of. Willaman, *et al*.......... 308
Sulfate, Determination of—in Sulfonated Oils. E. J. Kern.......... 785
Sulfates: Equilibria in Solutions Containing Mixtures of Salts—II. W. C. Blasdale.......... 164
Sulfates: Formation of Double Salts of Calcium and Potassium Sulfates at 100° C. E. Anderson and R. J. Nestell.......... 243
Sulfonation, Use of Catalysts in—of Aromatic Compounds. J. A. Ambler and W. J. Cotton.......... 968
Sulfonic Acids, Naphthalene. (*See* Naphthalene Sulfonic Acids)
Sulfur:
  Desulfurizing Action of Hydrogen on Coke. A. R. Powell.......... 1077
  Determination of Minute Quantities of Oil in Sulfur. L. S. Bushnell and H. S. Clark.......... 485
  Determination of—Forms in Coal. A. R. Powell.......... 887
  Determination of True Free—and True Coefficient of Vulcanization in Vulcanized Rubber. W. J. Kelly.......... 875
  Detection of Arsenic in Sulfur. H. S. Davis and M. D. Davis..... 479
  In Benzene. Note.......... 390
  Monochloride, Method for Determining—Content of Mustard Gas-S_2Cl_2 Mixtures. W. A. Felsing, S. B. Arenson and F. J. Kopp.......... 1054
  Monochloride, Pressures Produced by Action of—upon β,β'-Dichloroethyl Sulfide. T. G. Thompson and F. J. Kopp.......... 1056
  New Method for Determination of—in Oils. (*See* page 612) C. E. Waters.......... 482
  Precipitation of—from Crude Mustard Gas by Means of Ammonia. W. A. Felsing and S. B. Arenson.......... 1065
  Pyrites and—in 1918. Smith. Gov. Pub.......... 305
  Rapid Method for Determination of—in Petroleum Oils. A. W. Christie and C. S. Bisson.......... 171
  Standardization of—Boiling Point. Mueller and Burgess. Gov. Pub.......... 99
  Study of Reactions of Coal—Sulfur in Coking Process. A. R. Powell.... 1069
Sulfuric Acid, Commercial, Rapid Method for Quantitative Determination of Arsenic in. A. A. Kohr.......... 580
Sulfuric Acid Manufacture. Note.......... 181
Sulfuric Acid, Manufacture in U. S. Wells and Fogg. Gov. Pub... 1221
Sulfuric Acid: Some American-Made Chemical Reagents. W. D. Collins.......... 800
Sulfuric and Nitric Acids, Freezing Points of Mixtures of. W. C. Holmes.......... 781
Sumac, American: Tanning Material and Dyestuff. Veitch, *et al.* Gov. Pub.......... 1221
Sunflower Silage. Neidig and Vance. Gov. Pub.......... 308
Surface Waters, Hardness of—of U. S. W. D. Collins.......... 1181
SWEDEN, CHEMICAL INDUSTRY AND TRADE OF. O. P. Hopkins....... 1045

TABLES, Rapid Preparation of. J. C. Witt.......... 591
Talc and Soapstone in 1918. Diller. Gov. Pub.......... 618
Tannery Wastes, Purification of. Hommon. Gov. Pub.......... 406
Tannic Acid. Tariff Act of 1913. Gov. Pub.......... 406
Tanning Materials, True Tanning Value of Vegetable. J. A. Wilson and E. J. Kern.......... 465
Tantalum in 1918. Hess. Gov. Pub.......... 823
Tariff Act of 1913, Acids of Paragraph I Provided for in. Gov. Pub. 406
Tariff Commission. Gov. Pub..........98, 406, 617, 723, 1138
Tariff Commission. Professor Bogert Declines. Editorial.......... 731
Tariff. Congressional Committee Hearings. Gov. Pub.......... 96
Tariff Regulation. Extract from the Federal Law Relating to Removal of "Country of Origin" from Imported Articles.......... 198
Tartaric Acid and Cream of Tartar. Tariff Act of 1913. Gov. Pub.. 406
Teachers, High School Chemistry, Advanced Work for. W. R. Teeters.......... 198
TECHNICAL ASSOCIATION OF PULP AND PAPER INDUSTRY:
  Fall Meeting, Saratoga Springs, N. Y., September 1 to 3, 1920. T. J. Keenan.......... 815
Technical Training, Value of—in Reconstruction of Industries. Address, Chicago Meeting, A. C. S. T. E. Wilson.......... 941
Telescopic Control Tube, Testing of Saccharimeters by Means of. C. A. Browne.......... 792
Tellurium. Hill. Gov. Pub., 304; 1919.......... 1139
Tellurium and Selenium. V. Lehner.......... 597
Tellurium: Health Hazard in Industry. Shie and Deedes. Gov. Pub. 617
Tensiometer, Airplane. Larson. Gov. Pub.......... 96
Tetranitroaniline: Stability of Tetryl. C. L. Knowles.......... 246
Textiles, Testing Mildew Resistance of. B. S. Levine and F. P. Veitch.......... 139
Thermal Analysis: Modified Rosenhain Furnace. Scott and Freeman. Gov. Pub.......... 99
Thermal Conductivity, Automatic Methods of Gas Analysis Depending upon. E. R. Weaver, P. E. Palmer, H. W. Frantz, P. G. Ledig and S. F. Pickering (*See* Shakespear, 1027).......... 359
Thermal Conductivity Method, Application of—to Automatic Analysis of Complex Mixtures of Gases. E. R. Weaver and P. E. Palmer. 894
Thermal Expansion of Insulating Materials. Souder and Hidnert. Gov. Pub.......... 408
Thermocouple, Needle Type, Some Improvements on—for Low Temperature Work. G. F. Taylor.......... 797
Thermocouples, Welding—in Electric Arc. J. C. McCullough....... 903
Thiocyanates, Determination of—in Ammoniacal Liquor, and Waste Liquor in By-Product Coking Industry. J. A. Shaw.......... 676
Thompson Method, Modification of—for Determination of Acetic Acid in White Lead. L. McMaster and A. E. Goldstein.......... 170
Thorium, Zirconium, and Rare-Earth Minerals, 1919. Schaller. Gov. Pub.......... 1033
Thymol, Synthesis of—from *p*-Cymene. M. Phillips and H. D. Gibbs.......... 733
Timber, Noninflammable. Note.......... 82
Tin in 1918. Knopf. Gov. Pub.......... 97
Tin Mining in Seward Peninsula, Alaska. Harrington. Gov. Pub. 97
Tin Plate, Use of Hydrogenated Oils in Manufacture of. W. D. Collins and W. F. Clarke.......... 149
Tin Solder Substitutes. Note.......... 390
Titanium. Hess. Gov. Pub., 823; 1917, 1138; 1918.......... 823
Titanous Chloride, Analysis of Aromatic Nitro Compounds by Means of. F. L. English.......... 994
TNT as Blasting Explosive. Munroe and Howell. Gov. Pub....... 824
Tobacco, American Production, Import, Export, and Consumption of. Gov. Pub.......... 98
Toluene and Isoprene, Thermal Decomposition of Turpentine with Particular Reference to Production of. S. A. Mahood.......... 1152
Tomato, Process of Ripening in—from Commercial Standpoint. Sando. Gov. Pub.......... 1139
Tomato Products, Modification of Howard Method for Counting Yeasts, Spores, and Bacteria in. H. M. Miller.......... 766
Toxic Action, Experiments on—of Certain Gases on Insects, Seeds, and Fungi. Neifert and Garrison. Gov. Pub.......... 1139
Toxic Gases, Use of—for Peach-Tree Borer. Blakeslee. Gov. Pub. 100
Toy Sets for Chemical Experiments. Editorial Note.......... 109
Trinitroxylene, Manufacture of—for Use as Substitute for TNT in Bursting Charges for High Explosive Shell. J. Marshall.......... 248
Tristearin, Some Anomalies in Solidification Point of. B. H. Nicolet. 741
Tungsten. Gov. Pub. Bibliography, 96; Congressional Committee Hearings, 96; in 1917, by Hess.......... 1138
Tungsten Ores. Gov. Pub., 617; Congressional Committee Report.. 303
Turbidimeter, New, for Solutions of Gelatin, Cellulose, and Varnishes. S. E. Sheppard.......... 167
Turpentine. Veitch and Grotlisch. Gov. Pub.......... 1222
Turpentine (Gum Spirits and Wood Turpentine), Recommended Specifications for. Gov. Pub.......... 408
Turpentine, Thermal Decomposition of—with Particular Reference to Production of Toluene and Isoprene. S. A. Mahood.......... 1152

ULTRAVIOLET Light, Action of—on Yeast-Like Fungi—I. B. Feuer and F. W. Tanner.......... 740
Ultraviolet Rays in Water Purification. Gov. Pub..........303, 1221
Unsaponifiable Matters. W. H. Low and W. D. Richardson (*See* THIS JOURNAL, 11 (1919), 1161).......... 713
Uranium. Hess. Gov. Pub. 1917, 1138; 1918.......... 823
Uranium, Analytical Chemistry of—and Its Separation from Other Rare Elements. C. A. Pierlé.......... 60

VALENCE, Chemical, Structure of Atoms and Its Bearing on. I. Langmuir.......... 386
Vanadium. Hess. Gov. Pub. 1917, 1138; 1918.......... 823
Vapor Composition of Alcohol-Water Mixtures. W. K. Lewis....... 496
Varnish for Insulating Material. Note.......... 83
Varnishes, Gelatin, and Cellulose, New Turbidimeter for Solutions of. S. E. Sheppard.......... 167
Varnishes, Use of Paracoumarone Resin in. W. W. King, F. W. Bayard and F. H. Rhodes.......... 549
Varnishes, Wearing Quality of Exterior—Compared with Their Physical and Chemical Analyses. W. T. Pearce.......... 552
Vegetable Tanning Materials, True Tanning Value of. J. A. Wilson and E. J. Kern.......... 465
Ventilation, Ozone in. Gov. Pub..........617, 1221
Vinegar, Orange: Its Manufacture and Composition. H. D. Poore. 1176
Viscosimeter, MacMichael Torsional. W. H. Herschel. (*See* MacMichael, 817).......... 282
Viscosity, Measurement of—of Pyroxylin Solutions. E. F. Higgins and E. C. Pitman.......... 587
Vulcanization, Action of Certain Organic Accelerators in—of Rubber. G. D. Kratz, A. H. Flower and C. Coolidge.......... 317
Vulcanization, Determination of True Free Sulfur and True Coefficient of—in Vulcanized Rubber. W. J. Kelly.......... 875
Vulcanization, Expansion of Rubber Compounds during. C. W. Sanderson.......... 37
Vulcanization, Reactions of Accelerators during. C. W. Bedford and W. Scott.......... 31
Vulcanized Rubber Articles, Some Microsections Cut from. H. A. Depew and I. R. Ruby.......... 1156
Vulcanized Rubber, Effect of Certain Accelerators upon Properties of. II. G. D. Kratz and A. H. Flower.......... 971

WALKER, W. H. Editorial Note.......... 1148
WAR DEPARTMENT. Gov. Pub.......... 1032
WASHINGTON LETTER. J. B. McDonnell..........90, 200, 299, 398, 507, 613, 718, 818, 926, 1028, 1133, 1215
Washington University, Fellowship at. Note.......... 298
Washington University, New Laboratories. Note.......... 1214
Washington Y. M. C. A., Chemical Laboratory and Lecture Room of. Note.......... 598
Water-Alcohol Mixtures, Vapor Composition of. W. K. Lewis...... 496
Water Analysis, Turbidity Standard of. Wells. Gov. Pub.......... 619
Water and Geology Resources of the Gila and San Carlos Valleys, Arizona. Schwennesen. Gov. Pub.......... 304
Water, Convenient Method for Determination of—in Petroleum and Other Organic Emulsions. E. W. Dean and D. D. Stark.......... 486
Water, Flow of—in Dredged Drainage Ditches. Ramser. Gov. Pub. 824
Water-Glass, Adhesive, Colloidal Method for Increasing Volume of. J. D. Malcolmson.......... 174
Water-Glass, Composition of—Solutions. W. Stericker. Note...... 1026
Water, Oil, and Gas, Geochemical Relations of—Sunset-Midway Oil Field, California. Part II. Rogers. Gov. Pub.......... 407
Water-Power Investigations in Southeastern Alaska. Canfield. Gov. Pub.......... 304
Water Purification, Ultraviolet Rays in. Gov. Pub..........303, 1221
Water Supply Chemicals, Shipment of. Gov. Pub..........823, 930, 1032
WATER SUPPLY OF THE AMERICAN EXPEDITIONARY FORCES. E. Bartow.......... 903
Water Supply, Pollution of City—Enjoined. Gov. Pub.......... 96
Water Supply, Public, at Schenectady, N. Y., Gastroenteritis and Typhoid Fever Caused by Pollution of. Horton. Gov. Pub...... 1221
Water Supply, Surface, of U. S. Grover, *et al.* Gov. Pub. 1917. Part I. North Atlantic Slope Drainage Basins; Part XI. Pacific Slope Basins in California; Part XII. North Pacific Slope Drainage Basins.......... 1220
  1917. Part II. South Atlantic Slope and Eastern Gulf of Mexico Basins; Part IV. St. Lawrence River Basin, 1918.......... 1139
  1918. Part II. South Atlantic Slope and Eastern Gulf of Mexico Basins.......... 1220
Waterproofing: Determination of Water Resistance of Fabrics. F. P. Veitch and T. D. Jarrell.......... 26
Waters, Mineral, in 1918. Ellis. Gov. Pub.......... 512
Waters, Natural, Relationship of Hydrogen-Ion Concentration of—to Carbon Dioxide Content. R. E. Greenfield and G. C. Baker, 989; Correction.......... 1214

Waters, Nitrate Content of Certain—Considered Bacteriologically Safe. M. S. Nichols 987
Watertown Arsenal. Gov. Pub 96
Weights and Measures. Gov. Pub 406, 723, 930
Weights and Measures, Household. Gov. Pub 100
Weights, Unit, for Purchase of Reagents. W. D. Collins 1206
Welding Thermocouples in Electric Arc. J. C. McCullough 903
Wheat, Effect of Freezing on Composition of. Blish. Gov. Pub 824
Wheat Seedlings, Effect of Lime upon Sodium Chloride Tolerance of. LeClerc and Breazeale. Gov. Pub 409
White Lead, "Porcelain." E. Euston 974
Wines, Red, and Fruit Juices, Acidimetry of. A. M. Macmillan and A. Tingle 274
Wire Rod Mill, New. Note 82
Women Chemists. Bureau of Vocational Information. Editorial Note 212
Wood Alcohol: Coöperative Caution. C. Baskerville 81
Wood Alcohol No Longer: Hereafter Methanol. C. Baskerville 910
Wood, Distribution of Certain Chemical Constants of—over Its Proximate Constituents. W. H. Dore 472
Wood Pulp. Gov. Pub 823
Wood Pulp. Porter. Gov. Pub 823
Wood Pulp, Nitrocellulose from. R. G. Woodbridge, Jr 380
Woods, Airplane, Effect of Kiln Drying on Strength of. Wilson. Gov. Pub 406
Woods, Coniferous, Proximate Analysis of. W. H. Dore 476
Woods, Determination of Cellulose in. W. H. Dore, 264; Correction 395
Woods, Observations on Determination of Cellulose in. S. A. Mahood. 873
Wool, Artificial. Note 390
WORKS AND LABORATORY ACCIDENTS 89, 199, 297, 507, 1026

XENON and Krypton, Spectra of. Merrill. Gov. Pub 99
Xylose: Sugar-Cane Fiber and Cottonseed Hulls, Acid Hydrolysis of. E. C. Sherrard and G. W. Blanco 1160

YALE University, New Chemical Laboratory for. Note, 1028; Editorial Note 1044
Yeasts, Spores, and Bacteria, Modification of Howard Method for Counting—in Tomato Products. H. M. Miller 766

ZIRCONIUM, Determination of—in Steel. G. E. F. Lundell and H. B. Knowles 562
Zirconium, Investigations on. J. W. Marden and M. N. Rich 651
Zirconium, Thorium, and Rare-Earth Minerals in 1919. Schaller. Gov. Pub 1033
Zinc: Gov. Pub 96, 722
  Alloy with Manganese. Note 389
  In 1917. Siebenthal. Gov. Pub 617
  Ore. Gov. Pub 406
  Oxide, Dry and Paste, Specifications for. Gov. Pub 408
  Oxide, Leaded, Specifications for. Gov. Pub 408
  Production (1917 and 1918). Gov Pub. Central States, by Dunlop and Butler; New Mexico and Texas, by Henderson, 97; Eastern States, by Hill; Nevada, by Heikes; Montana, by Gerry; New Mexico and Texas, by Henderson; Arizona, by Heikes; California and Oregon, by Yale; Idaho and Washington, by Gerry; Colorado, by Henderson, 407; Utah, by Heikes, 512; Colorado, by Henderson 1138
  Reductor, Application of Rotating—in the Determination of Molybdenum. W. Scott 578
  Reflective Properties of Alloys of—and Magnesium with Aluminum. Waltenberg and Coblentz. Gov. Pub 409

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